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THE DIFFUSION HALOES OF THE IRIDESCENT FELDSPARS

By Sir C. V. Raman and A. Jayaraman
(*From the Raman Research Institute, Bangalore*)

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1. Introduction

By reason of the brilliance and variety of the optical effects displayed by it and its availability in large sizes, labradorite is easily the most spectacular amongst the iridescent feldspars. The explanation of its remarkable behaviour had long remained rather mysterious and hence it was taken up for investigation at this Institute. In a paper published in these *Proceedings*,[1] the results of our studies made with numerous specimens of this material were described and the explanation of the optical behaviour of labradorite to which they led unambiguously was also set out. In a further paper published shortly afterwards,[2] the optical behaviour of the Ceylon moonstones was studied and discussed. These two cases, however, do not exhaust the list of feldspars which show interesting optical effects. Professor Ito of the Mineralogical Institute of Tokyo very kindly presented us with a collection of the small but beautifully crystallised moonstones from Korea. Through the kindness of Prof. T. N. Muthuswamy of Madras, we have also received a collection of quite large pieces of plagioclase feldspar from Gudur in South India exhibiting a blue or bluish-white iridescence. Some kind friends also enabled one of us to visit the pegmatite areas in the Coimbatore District in South India, and to make a collection of specimens of the orthoclase feldspar exhibiting a golden-yellow schiller found in that area. Other varieties of feldspar exhibiting "Labradorescence" are described in a memoir by Boggild.[3] But these were not available to us.

A feature common to all the varieties of feldspar mentioned above and studied by us is that the light entering the material and returned from its interior is not a true optical reflection but is a *diffusion of light* spread over a range of angles. The study of the features of this diffusion is of great importance for obtaining a definite idea of the structure responsible for the iridescence of the feldspar. A convenient method of carrying out such studies was devised and described by one of us two years ago.[4] The technique adopted is to illuminate a *small area* of the specimen by a narrow

intense beam of light and to receive the radiation diffused from it on a white screen held not at too great a distance therefrom. The observations have to be made in a darkened room, and the more intense the incident pencil of light is, the more striking are the observed effects. By altering the spot on the specimen which is illuminated, or by tilting the specimen with respect to the direction of the incident pencil of light, one can quickly observe the resulting changes in the pattern of the diffused light. The disturbing effects arising from refraction and scattering at the external surface of the specimen may be eliminated completely by immersing it in a glass cell containing a transparent liquid of suitable refractive index which is traversed by the incident beam. If, however, the external surface of the specimen has been suitably cut and polished, the disturbing effects are less troublesome and such immersion is not so essential except when the polished surface is curved, in which case the effects of refraction cannot otherwise be got rid of. In all cases, the diffusion pattern may be photographed by receiving it on a sheet of bromide paper suitably held.

2. THE DIFFUSION HALOES OF LABRADORITE

The summary of our paper on labradorite referred to above is reproduced below *in extenso*, since the actual facts of observation as well as their theoretical explanation are clearly stated therein.

"General considerations indicate that the phenomenon of labradorescence owes its origin to the segregation of potash feldspar as crystallites or lamellæ of orthoclase which remains embedded in an albite-anorthite matrix and give rise to optical heterogeneity. The following are derived as theoretical consequences of such segregation and have been confirmed by observations made with a representative collection of specimens.

(A) Labradorite which is multiply-twinned according to either the albite or pericline law or both, exhibits its characteristic reflections in two different settings geometrically related to each other by the twinning law. The two reflections display identical colours, but have their origins in different parts of the crystal, and this makes itself evident as a visible banding in one or the other or both of the reflections.

(B) The light reflected transversely to the incident beam is completely polarised.

(C) The intensity of the reflected light is independent of the setting of the reflecting layers in their own plane.

(D) The spectral character of the reflected light would approach that of a Tyndall diffusion when the crystallites are very small. Hence the

colours of the first order in the Newtonian sequence would not be observed. The spectral character and the colour sequence at the later stages of segregation would also be different from those of thin films.

(E) The angular spread of the reflected light is greatest for the blue iridescence and less for other colours such as yellow, orange and red.

The effects arising when labradorite is illuminated and observed by polarised light are also described and explained in the paper. Numerous photographs reproduced in five plates illustrate the observed phenomena."

The terms " reflections " and " reflected " used in the foregoing summary of our earlier paper are rather misleading and should be replaced by " diffusion haloes " and " diffused " respectively. Indeed, the angular spread of the blue labradorescence exhibited by the finest specimens is so large that it would be erroneous to describe the phenomenon as a reflection.

Figures 1, 2 and 3 in Plate I accompanying the present paper were recorded respectively with the specimen 3, and with two different areas of the specimen 5 referred to on pages 13 and 14 of our earlier paper. The photographs display in a striking manner the distinctive features of the optical behaviour of labradorite, and would have been even more striking had they been recorded and reproduced in full colour. It would then have been evident that the two haloes seen in each figure are of identical colour and that the aventurine reflection seen midway between them is white. In Figs. 4, 5 and 6 of Plate III and Figs. 6, 7 and 8 of Plate IV of our earlier paper, photographs of the same two specimens as viewed from different directions were reproduced. They show that both of these specimens exhibit a visibly banded labradorescence, arising from the fact that the polished face of the specimen was nearly parallel to the crystallographic B-planes and hence that the effects due to both sets of orthoclase lamellæ present in the twinning layers of the plagioclase feldspar can be observed at the same setting. In the present method of study, the light diffused by these two sets of layers in different directions is recorded simultaneously, one on either side of the aventurine reflection; the latter is produced by the plates of hæmatite included in the feldspar and as these have their faces parallel to the B-planes, the reflection by them indicates the position of these planes. In the case of these specimens, it is noticed that when the illuminated area is caused to traverse the bands of labradorescence, the intensity of one of the diffusion haloes fluctuates relatively to that of the other. The character and intensity of the haloes and their relative positions as recorded in the figures of Plate I of the present paper thus completely demonstrate the statement (A) quoted above from the earlier paper.

It will be seen further that the haloes appearing in Plate I are of different sizes. Their colours as observed visually were also different. The haloes recorded in Fig. 1 had a golden yellow colour, in Fig. 2 a greenish-blue colour, while in Fig. 3 they were blue. This correlation of the spectral character of the labradorescence with the angular dimensions of the diffusion haloes is further confirmed by the series of five diffusion haloes photographed with other specimens and reproduced as Figs. 1 to 5 in Plate II. Figure 1 which shows the largest halo was of a deep blue labradorescence, while the remaining haloes exhibited respectively a light blue, greenish-blue, yellow, and red colour. The progressive diminution in the angular spread of the diffusion haloes with the shift of the maximum intensity towards the red end of the spectrum (stated as proposition E in the summary quoted above) is thus completely confirmed. We shall return presently to a consideration of its theoretical significance.

As is to be expected, the colour of the diffusion haloes changes with the angle of incidence of the light on the lamellæ responsible for the labradorescence. Such incidence may be altered by a change in the setting of the specimen with reference to the incident light. The range of incidences attainable is however limited by reason of the refraction of light at entry into the specimen, by the inclination of the lamellæ to the polished face, and also by reason of refraction of the diffused light at emergence. Thus, it is often the case that one of the haloes ceases to be observable at a particular setting of the crystal, and that a different setting is necessary to enable it to be seen. To avoid this difficulty, it is helpful to immerse the specimen in a cell containing a suitable liquid. The range of incidences attainable is thereby greatly increased and the change in colour of the halo with the angle of incidence of the light is more readily observable. Indeed, with this arrangement, the angle of incidence of the light on the orthoclase crystallites present in the alternate layers of the albite twinning may be so different that the two haloes appear with altogether different colours.

The other results (B) and (C) stated in our earlier paper, namely, the polarisation of the labradorescence and the independence of its intensity on the azimuth of incidence can likewise be demonstrated objectively by the present method of study. The polarisation of the diffused light is only complete in a direction transverse to the incident beam and to enable it to be demonstrated, it is necessary to immerse the specimen in a suitable liquid. The specimen should also be orientated within the cell in such manner that the depolarising effect of its birefringence is a minimum. A polaroid is then interposed between the feldspar and the receiving screen

and rotated. The intensity of the diffusion halo undergoes large variations; the extinction observed is fairly complete for a deviation of 90° from the direction of the incident light.

The study of the diffusion haloes of labradorite thus completely confirms the findings reported in our earlier paper, and there is no need to traverse here the question of the origin of labradorescence already fully dealt with by us. It is sufficient to quote the remark made earlier that the colours of labradorite are neither a simple Tyndall diffusion nor a simple case of thin-film colours, but a special phenomenon in the elucidation of which the principles underlying both play a part. When the crystallites of orthoclase which segregate themselves from the albite-anorthite matrix are of very small size, they give rise to a Tyndall effect with the shorter wave-lengths predominating and hence exhibiting a rich blue colour. On the other hand, if they are not small in comparison with the wave-length of light and are assumed on the basis of the observed facts to be lamellæ having a specific orientation in the crystal, the colour of the diffracted light would be determined by their thickness while its angular extension would depend on their other dimensions. That the colour of labradorescence shows a definite correlation with the size and shape of the diffusion haloes strongly supports the proposed interpretation. On the basis of such an explanation and the observed shape, colour and angular extension of the diffusion haloes, it is possible to make a rough estimate of the linear dimensions of the orthoclase lamellæ. The figures are given below in Table I.

TABLE I

Colour of Labradorescence	Thickness of the crystallites	Lateral dimension	Greatest dimension
Deep blue ..	0·1 μ	1 μ	2 μ
Green ..	0·2 μ	2 μ	3 μ
Orange-yellow ..	0·4 μ	4 μ	5 μ
Red ..	0·5 μ	6 μ	9 μ

The difference between the refractive indices of the orthoclase lamellæ and the surrounding albite-anorthite matrix is about 0·04. On multiplying the dimensions of the crystallites by this quantity, the retardation produced in a light wave travelling in a direction normal to the lamellæ is seen to be only a small fraction of the wave-length of light, and hence one could scarcely hope to be able to distinguish the individual lamellæ under the

microscope. The confusion due to the presence of great numbers of them, and the presence of the visible inclusions which give rise to the aventurine reflection have also to be taken into consideration. They would diminish the prospect of success in observing the individual crystallites of orthoclase even with the aid of modern phase-contrast methods. On the other hand, if the crystallites are looked at edge-wise, the possibility of discovering their presence under the microscope would be greater.

3. PLAGIOCLASE FELDSPAR FROM GUDUR (SOUTH INDIA)

This material of which a large collection has been made for the Museum of this Institute is an opaque white feldspar. Many of the specimens however show a distinct iridescence, varying in colour from a delicate blue to a brilliant white. Only occasionally is a hint of any other colour noticeable. As cleavage faces are frequently seen, there is no difficulty in verifying that the iridescence is noticed on the exposures of the B-face of the crystal. From the character of the iridescence, it is quite clear that the material is a plagioclase feldspar. The iridescence is seen in two different settings of the crystal with reference to the incident beam and the direction of observation; the areas which appear bright in one setting are dark in the other and *vice-versa*. The angle of rotation of the specimen needed is of the same order of magnitude as in the case of labradorite. But in other respects this feldspar behaves differently from labradorite. The colours are much less saturated and much less varied in hue. Further, whereas in the case of labradorite the change from one setting to the other is brought about by a rotation of the specimen about a line in the B-face making an angle of 70° with the *a*-axis, in the present case the rotation required is about the *a*-axis itself. There is also visible evidence of twinning, sometimes of the albite type, sometimes of the pericline type and sometimes of both. It seems probable from what has been stated that the chemical composition of the feldspar is principally albite and that the iridescence arises from the presence of internally segregated lamellæ of orthoclase. These are inclined to the B-face as in the case of labradorite but in a different azimuth altogether.

The diffusion haloes of this variety of feldspar are readily observed. They appear in pairs, one on either side of the ordinary optical reflection from the B-face. The relative intensity of the two haloes is very variable and depends upon the position of the illuminated spot on the crystal face. The angular dimensions of the haloes are rather small and the indications are that they vary with the colour, being larger for the blue and less for the bluish-white haloes. We have not however made any quantitative

measurements under appropriate conditions. It has been noticed that, as in the case of labradorite, the diffusion halo is strongly polarised when it is observed in a direction perpendicular to the incident beam.

4. The Diffusion Halo of the Ceylon Moonstones

The optical phenomenon familiarly known as schiller is exhibited by certain varieties of orthoclase feldspar, amongst which the best known are the moonstones from Ambalangoda in Ceylon of which there is a large collection in the Museum of this Institute. The optical characters of the schiller vary enormously with the individual specimens in spite of the fact that all of them come from the same area. At one extreme, we have the moonstones exhibiting a schiller of a beautiful blue colour; at the other extreme, we have those which give a schiller of great brilliance and of a perfectly white colour. In the paper which appeared earlier in these *Proceedings* and has already been referred to, the explanation of these effects was described and discussed in great detail. The conclusion reached was that the schiller is essentially a diffusion of light within the crystal and that such diffusion is a consequence of local fluctuations in the composition of the crystal. In other words, the relative proportion of the soda and potash feldspars in their composition (the latter being the principal constituent) varies from point to point. The same situation is described by the statement that the soda feldspar tends to segregate itself from the potash and form tiny crystallites which orientate themselves regularly in the lattice; by reason of the difference in refractive indices of albite and orthoclase, the crystal becomes optically heterogeneous and a diffusion of the light results. The lattice spacings of albite and orthoclase differ substantially along the *a*-axis and much less so along the other two axes. In consequence, the albite crystallites may be expected to spread out principally along the *b* and *c* axes in preference to the *a*-axis. The diffusion of light would therefore tend to be non-uniform with respect to direction.

Thus, there is a parallelism between the optical effects exhibited by labradorite and by the Ceylon moonstones. But there are also notable differences which are readily intelligible in the light of the different circumstances in the two cases. The Ceylon moonstones, unlike labradorite, exhibit only a single diffusion halo, the same being elliptic in shape. The angular dimensions of the halo vary enormously with the colour of the schiller. It is very large for the moonstones exhibiting a blue schiller, smaller and brighter for those exhibiting a bluish-white schiller, and smallest and brightest with those exhibiting a pure white schiller. Photographs of the haloes in these three cases have already been reproduced in

the article in *Current Science* cited as reference 4. From the angular dimensions of the halo in each case, the dimensions of the crystallites responsible for them can be roughly evaluated. The figures which are the averages derived from a large number of specimens are given below in Table II.

TABLE II

Colour of schiller	Major axis	Minor axis
Blue ..	1·6 μ	0·8 μ
Bluish white ..	3·0 μ	1·6 μ
White ..	6·0 μ	5·0 μ

It may be remarked that the measurements were made with moonstones immersed in a cell of liquid and with a pencil of light traversing them in each case along the schiller axis, that is to say, along the direction in which the schiller is most prominent. Actually, the diffusion haloes may also be observed when the light traverses the moonstone in other directions. The colour and intensity of the schiller and other attendent effects alter with the angle of incidence. The study of these phenomena opens up an extensive field for research, but we do not propose to enter into the same here.

The dimensions shown in the second and third columns of Table II are transverse to each other and to the direction of the schiller axis. The question whether crystallites of the dimensions shown could be observed directly under the microscope is one of considerable interest. A factor that needs to be considered in this connection is the difference in the refractive indices of the crystallites and of the surrounding medium. This difference for the three principal directions is respectively 0·015, 0·010, 0·010. Multiplying these by the linear dimensions shown in Table II, it is seen that the retardation in phase produced by a single crystallite with reference to the surrounding medium would lie between 0·01 μ and 0·02 μ for a blue schiller and between 0·07 μ and 0·1 μ for a white schiller. These optical retardations are much smaller than a wave-length of light and when it is recalled that the effects of a great number of crystallites would overlap, it will be evident that there is scarcely any possibility of the individual elements responsible for the diffusion of light being distinguishable under the microscope. We are thus justified in stating that the schiller of moonstones has its origin in a heterogeneity incapable of being resolved by ordinary microscopic examination. The view put forward by some

mineralogists, notably E. J. Spencer,[5] that the schiller of moonstones is due to a microperthetic or lamellar structure is thus clearly untenable. The optical irregularities reported by the same author as observable under special conditions of illumination are of much larger dimensions than those noted in Table II. They obviously cannot be responsible for the observed schiller.

5. The Diffusion Haloes of the Korean Moonstones

The chemical composition of a typical moonstone from Korea has been reported by Professor Ito.[6] It is given as 7·32% of K_2O and 6·88% of Na_2O, while a typical Ceylon moonstone is reported to contain 11% K_2O and 3·8% Na_2O. It is not surprising in these circumstances that some differences are observed between the optical behaviour of the Ceylon and the Korean moonstones. We find the latter to fall into two categories, namely, those exhibiting a bright blue schiller and the others a bluish-white schiller. The most remarkable difference between the Ceylon and the Korean moonstones is, however, that the latter are sometimes twin-crystals and sometimes quartets. Whereas an individual crystal exhibits only a single diffusion halo, a twin crystal shows two, while a quartet shows four haloes. The first case is illustrated in Fig. 1 of Plate III and the second case in two different settings of the moonstone in Fig. 2 of Plate III and Fig. 2 of Plate IV respectively. The quartet of haloes exhibited by a moonstone containing four components is illustrated in Fig. 1 of Plate IV.

6. The Coimbatore Moonstones

The material with which some observations were made and are reported here was collected from the Kangayam area of the Coimbatore District in South India. From its observed crystallographic characters, it would appear that it is an orthoclase feldspar. Some specimens are translucent with a pale brownish tint. Other examples are however forthcoming which are much more transparent and exhibit a pale greenish hue. These specimens have a perfect C-cleavage, and plates of the material parallel to that cleavage can therefore be obtained suitable for optical investigation. A very interesting property of the greenish moonstones is they exhibit a schiller which in many cases has a golden yellow colour, while in others it is yellowish-white. We have not as yet made any quantitative studies, but from general inspection, it would seem that the position of the schiller axis for this variety of moonstone is approximately the same as for the Ceylon moonstones. The character of the diffusion halo is however notably different. The halo in the present case is rather small in area and exhibits the same colour as the schiller itself. A special feature is the appearance of a bright

cross whose arms pass through the diffusion halo and extend in directions perpendicular to each other. We have also noticed that when the moonstone is set so that the characteristic schiller appears in a direction transverse to the incident light, the diffusion halo is almost completely polarised. Another remarkable property of this moonstone is the polarised extinction of light which it exhibits in certain circumstances. This effect is of the same general nature as that described on pages 135 and 136 of our earlier paper on the Ceylon moonstones,[2] but is much more conspicuously observable.

SUMMARY

Labradorite, the moonstones from Ceylon and Korea and other varieties of feldspar exhibiting iridescence have been investigated, and in all cases it has been found that such iridescence is the consequence of a diffusion of light within the material and not a true optical reflection. By a suitable technique, the diffusion haloes can be photographed and from their geometric positions, colour and angular dimensions, important conclusions can be drawn regarding the structures responsible for the iridescence. The plagioclase feldspars usually show two haloes geometrically related to each other according to the twinning law. The Ceylon and Korean moonstones differ in this respect; while the former invariably shows only one halo, the latter exhibits one, two or four according to the number of components present in the individual crystal.

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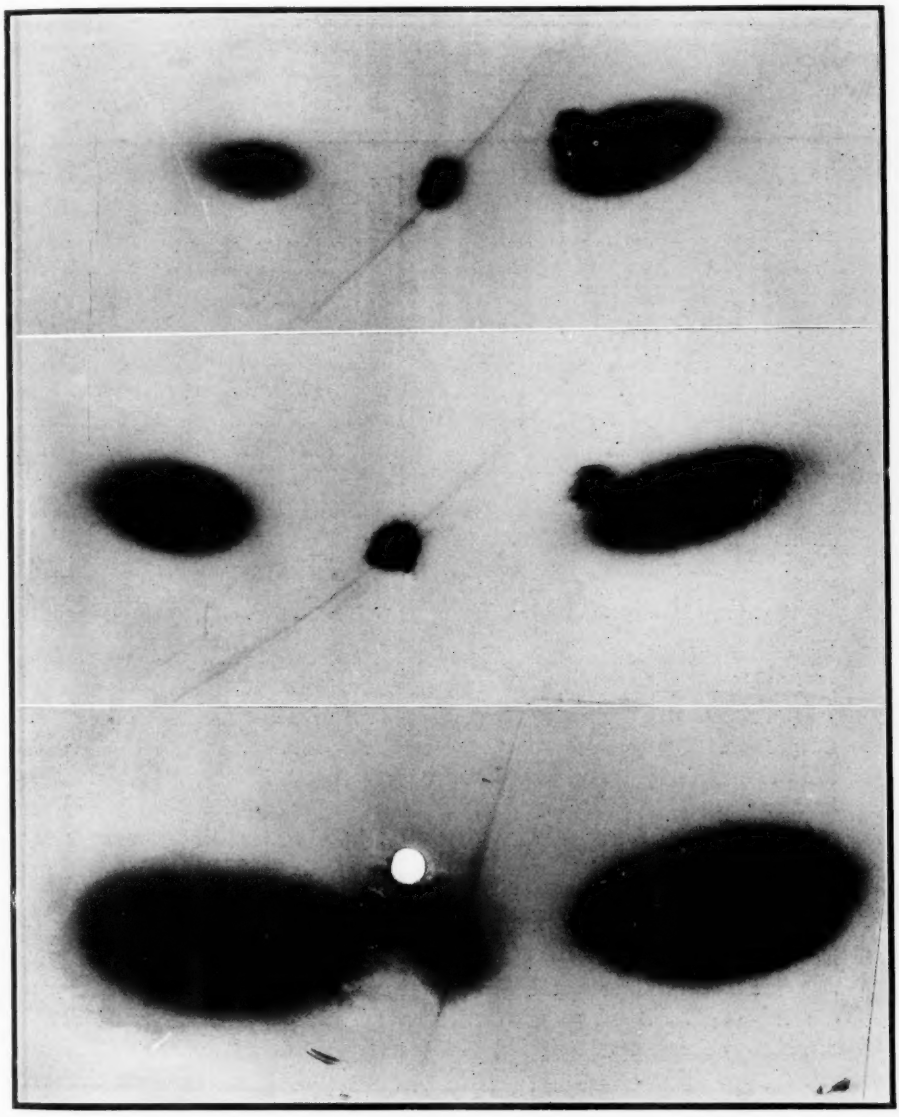


FIG. 1

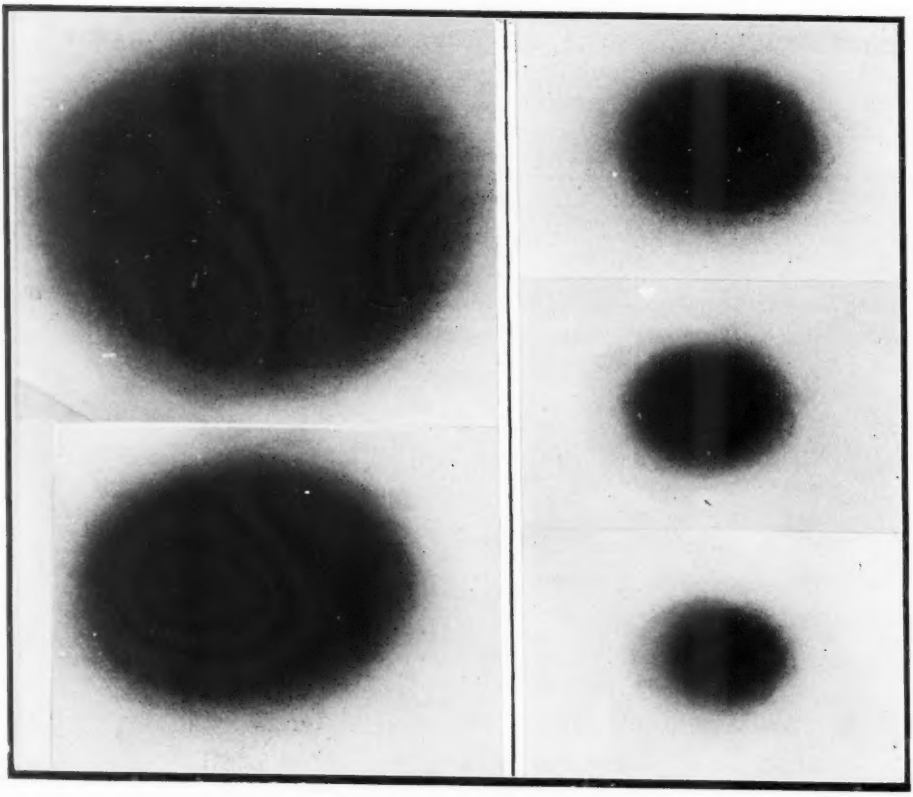
FIG. 2

FIG. 3

Diffusion Haloes of Labradorite

FIG. 1

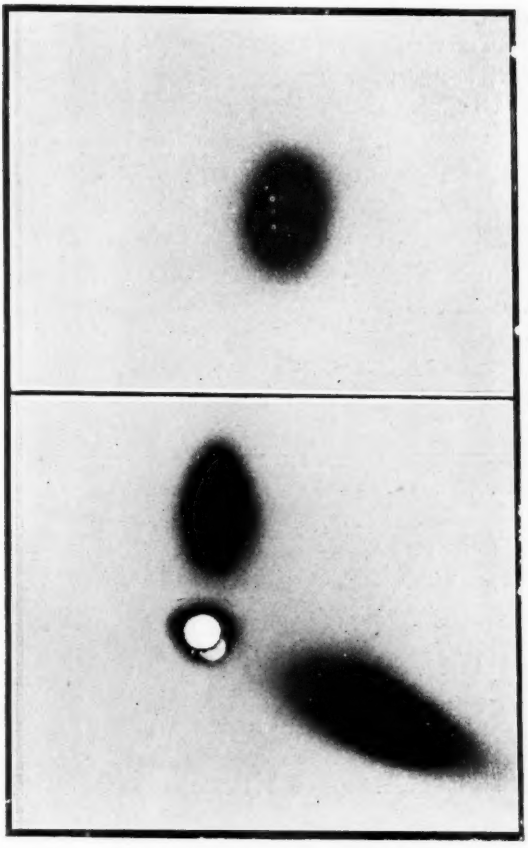
FIG. 2



Diffusion Haloes of Labradorite

FIG. 1

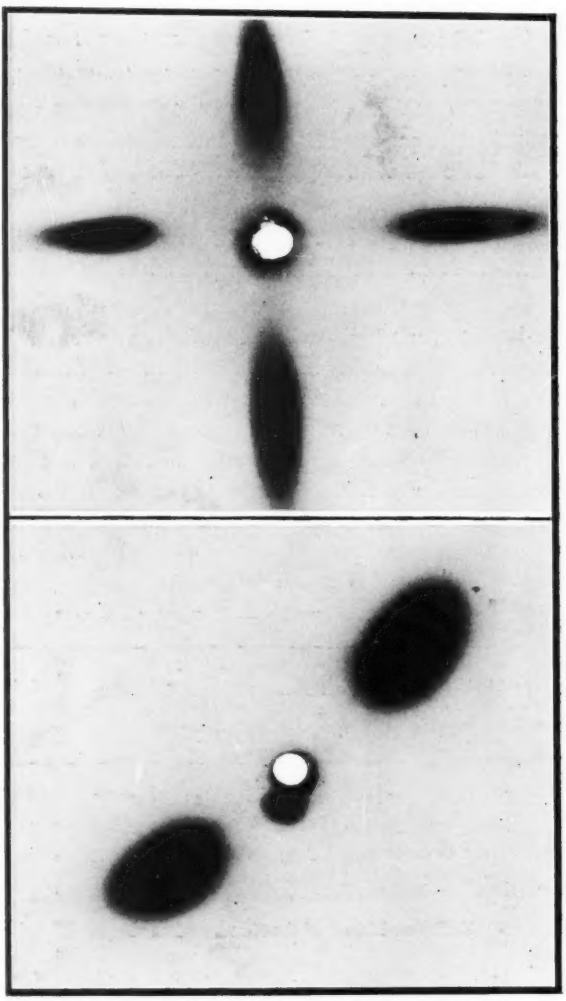
FIG. 2



Diffusion Haloes of the Korean Moonstones

FIG. 1

FIG. 2



Diffusion Haloes of the Korean Moonstones

STUDIES IN THE CHEMICAL BEHAVIOUR OF SOME COMPOUNDS OF SULPHUR

Part IV. Reaction Between Hydrogen Iodide and Some Esters of Oxy-Acids of Sulphur

By A. R. Vasudeva Murthy

(*Indian Institute of Science, Bangalore*)

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Though thiosulphurous acid has not been isolated so far, its esters have been prepared. Isolation of its anhydride has been reported.[1, 2] Lengfeld[3] prepared in 1895, the methyl and ethyl esters of the acid. In 1926, the use of diethyl thiosulphite as a vulcanising agent was patented.[4] Meuwsen[5] in his study of the two esters claimed the existence of isomeric forms. Stamm[6] however, showed that there were no isomers and that the faulty observation of Meuwsen[5] was due to sulphur chloride as an impurity. Stamm and Wintzer[7] studied the hydrolysis of the two alkyl thiosulphites. Stamm and Goehring[8] examined their oxidising action on hydrogen iodide obtained by dissolving potassium iodide in anhydrous formic acid. It has been shown by the present author[9] that the technique employed by Stamm and Goehring in studying the oxidising action was unsatisfactory. The present paper deals with the reactions of the esters with hydrogen iodide, eliminating the use of formic acid which introduces complications, by causing side reactions.

Experimental

Preparation of the Esters.—Alkyl thiosulphites: Alcohol-free sodium ethylate and methylate were prepared by Claisen's method.[10] The purity of ethylate was 99·6% and that of the methylate 99·3%.

A 10% solution of purified sulphur chloride in petroleum ether (B.P. 30°–40° C.) was cooled to − 10° C., and was carefully treated with the calculated quantity of sodium alcoholate, as recommended by Stamm.[6] The resulting ester was purified by redistillation under vacuum. The boiling points of the esters were:

	B.P.
Methyl thiosulphite	35° C. (at 17 mm. of Hg)
Ethyl thiosulphite	63–65° C. (at 15–16 mm. of Hg)

The purity of the esters was further checked by determining their sulphur content as barium sulphate. Sulphur present in the esters was:

	Theoretical	Experimental
Methyl thiosulphite ..	50·80%	50·55%
Ethyl thiosulphite	41·56%	41·24%

In storing, the esters were carefully protected from moisture.

Diethyl Sulphite.—Diethyl sulphite was prepared by treating pure thionyl chloride with the calculated amount of absolute ethyl alcohol, in a rapid stream of carbon dioxide, as suggested by Voss and Blanke.[11] On removal of hydrogen chloride, the ester was purified by distillation in an all-glass apparatus.

Boiling point (154° C. at 685 mm. of Hg) and density (1·1059–25° C.) measurements, as well as sulphur determinations showed that the ester was at least 99·5% pure.

Reaction between Hydrogen Iodide and the Esters.—Known weights of the esters, in dilute carbon tetrachloride (or benzene) solution were introduced into bulbs containing hydrogen iodide. The reaction was rather slow. At first there was a yellowish red colour. This finally turned to the characteristic purple of iodine in carbon tetrachloride (after nearly an hour). The products of reaction were hydrogen sulphide and iodine. These were estimated by methods described in an earlier paper.[9] The results are given in Tables I and II.

TABLE I

Action of Hydrogen Iodide on Methyl Thiosulphite

Sl. No.	Methyl thiosulphite taken*	H_2S obtained	Iodine obtained in g. atom $\times 10^6$ per g. soln.	Ratio of Iodine to hydrogen sulphide	Elemental sulphur	% of Ester reduced to H_2S	% Ester reduced to S	% Ester accounted for
1	5·68	5·56	17·05	3·07	..	97·9	..	97·9
2	9·87	9·63	29·16	3·02	..	97·6	..	97·6
3	14·45	14·25	42·25	2·97	..	98·4	..	98·4
4	18·32	18·12	55·12	3·04	..	98·9	..	98·9
5	168·96	32·69	168·1	..	34·86	47·4	50·5	97·9
6	172·27	5·85	350·2	..	163·6	3·4	94·9	98·3

* Quantities of sulphur and its compounds are expressed in terms of g. atom of S $\times 10^6$ per g. of solution.

TABLE II

Action of Hydrogen Iodide on Ethyl Thiosulphite

Sl. No.	Ethyl thiosulphite taken*	H_2S obtained	Iodine obtained in g. atom $\times 10^6$ per g. soln.	Ratio of Iodine to hydrogen sulphide	Elemental sulphur	% of Ester reduced to H_2S	% Ester reduced to S	% Ester accounted for
1	4·53	4·38	13·05	2·98	..	96·7	..	96·7
2	11·38	11·05	33·25	3·01	..	97·1	..	97·1
3	15·16	14·98	45·16	3·08	..	98·8	..	98·8
4	19·43	19·15	58·15	3·04	..	98·5	..	98·5
5	72·48	34·56	186·5	..	37·78	47·8	51·5	99·3
6	196·37	8·96	397·6	..	183·9	4·6	89·4	94·0

* Quantities of sulphur and its compounds are expressed in terms of g. atom of S $\times 10^6$ per g. of solution.

The results show that when iodide is in large excess, the thiosulphite is completely reduced to hydrogen sulphide, with a moderate excess of hydrogen iodide however, only a part of the thiosulphite is reduced to hydrogen sulphide, the rest being converted to sulphur. Hydrogen iodide in still smaller quantities, yields very little hydrogen sulphide. Considerable difficulty is experienced in estimating accurately the liberated sulphur as it firmly adheres to the glass surface.

When there is complete reduction of thiosulphite to hydrogen sulphide, the ratio of sulphur (as hydrogen sulphide) to iodine is 1 : 3. The overall reaction is:

$$S_2(OR)_2 + 6HI \rightarrow 2H_2S + 2R - OH + 6I$$
$$(R = C_2H_5 \text{ or } CH_3).$$

The reaction takes place in stages and spectrophotometric evidence obtained by the author (and discussed in a later paper) has shown that sulphur iodide is the intermediate compound. The yellowish red colour formed during the earlier stages of the reaction has been found to be due to sulphur iodide. When hydrogen iodide is in large excess and the ester is in dilute solution, the sulphur iodide is completely reduced to hydrogen iodide. If hydrogen iodide, however, is only in moderate excess, part of the sulphur iodide escapes further reduction, but is decomposed into sulphur and iodine. With higher concentration of ester in carbon tetrachloride solution, there is partial decomposition of the sulphur iodide even though hydrogen iodide may be in considerable excess.

In their study of the reduction of alkyl thiosulphites by hydrogen iodide, Stamm and co-workers employed formic acid solutions of potassium iodide. The formic acid present might have catalytically decomposed sulphur iodide very rapidly and conditions thus were not favourable for further reduction of sulphur iodide to hydrogen sulphide. In estimating the iodine liberated, Stamm and co-workers[8] added water to the reaction mixture. In presence of water any hydrogen sulphide formed present would readily be oxidised by iodine to sulphur. This was partly responsible for their failure to detect hydrogen sulphide among the products of reaction.

The present author has carried out the reaction of the two thiosulphites with formic acid solutions of potassium iodide and finds that hydrogen sulphide is among the products of reaction. Results are given below in Tables III and IV.

TABLE III

Reaction between Potassium Iodide in Formic Acid and Methyl Thiosulphite

Expt. No.	Methyl thiosulphite*	H_2S obtained	Iodine liberated in g. atom $\times 10^6$	Elemental sulphur	% Ester reduced to H_2S	% Ester reduced to S	Total S accounted for
1	8·96	3·65	22·52	5·26	40·7	58·7	99·4
2	12·58	5·96	31·72	6·58	47·4	52·3	99·7
3	16·26	6·85	39·86	9·32	42·1	57·3	99·4
4	19·64	7·96	46·36	11·15	40·5	56·8	97·3

* Quantities of sulphur and its compounds have been expressed in terms of g. atom of S $\times 10^6$ per g. of solution.

TABLE IV

Reaction between Potassium Iodide in Formic Acid and Ethyl Thiosulphite

Expt. No.	Ester taken* (Ethyl)	H_2S obtained	Iodine liberated in g. atom $\times 10^6$ per g. of solution	Elemental sulphur	% Ester reduced to H_2S	% Ester reduced to S	Total S accounted for
1	6·36	2·38	14·93	3·86	37·4	60·7	98·1
2	8·58	3·49	21·68	4·98	40·6	58·0	98·6
3	11·86	4·86	29·25	6·85	40·9	57·7	98·6
4	16·89	7·48	39·56	9·15	44·3	54·2	98·5

* Quantities of sulphur and its compounds have been expressed in terms of g. atoms of S $\times 10^6$ per g. of solution.

The reduction of diethyl sulphite by hydrogen iodide has also been studied and the results are given in Table V.

As with thiosulphites the alkyl sulphite is also completely reduced to hydrogen sulphide, provided the solution is dilute and hydrogen iodide is in large excess. For every g. mole of sulphur formed as hydrogen sulphide, 6 g. atoms of iodine are liberated, the reaction being

$$(EtO)_2SO + 6HI \rightarrow H_2S + 2EtOH + H_2O + 6I.$$

TABLE V

Reaction between Hydrogen Iodide and Diethyl Sulphite

Expt. No.	Ester taken*	H_2S obtained	SO_2	Elemental sulphur	Iodine liberated in g. atom $\times 10^6$ per g. of solution	Ratio of $I_2 : H_2S$	% Ester reduced to H_2S	% SO_2	% S	Total ester accounted
1	4·47	4·25	..	..	25·75	6·06	95·1	..	..	95·1
2	7·38	7·26	..	..	43·83	6·03	98·3	..	..	98·3
3	11·56	11·38	..	..	68·42	6·01	98·4	..	..	98·4
4	15·84	15·66	..	..	94·56	6·03	98·9	..	..	98·9
5	72·56	29·56	21·25	20·98	268·3	..	40·7	29·3	28·9	98·9
6	158·28	5·89	75·30	76·90	350·8	..	3·7	47·6	48·6	99·9

* Quantities of sulphur and its compounds are expressed in terms of g. atoms of S $\times 10^6$ per g. of solution.

As with the thiosulphites, there is a yellowish red colour in the early stages of the reaction. Thionyl iodide is found to be the intermediate product as shown by spectrophotometric studies. In presence of a large excess of hydrogen iodide the thionyl iodide is reduced to hydrogen sulphide in the final stage of reduction. When hydrogen iodide is in moderate excess, part of the thionyl iodide decomposes to yield sulphur dioxide, sulphur and iodine[12]:

$$2SOI_2 \rightarrow SO_2 + S + 4I$$

The sulphur dioxide formed may react with hydrogen iodide producing sulphur.

Similar results were obtained when dilute solutions of dimethyl sulphate were treated with hydrogen iodide.

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STUDIES IN THE CHEMICAL BEHAVIOUR OF SOME COMPOUNDS OF SULPHUR

Part V. Reaction Between Hydrogen Iodide and Chlorine Compounds of Sulphur

By A. R. Vasudeva Murthy

(*Indian Institute of Science, Bangalore* 3)

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M. R. A. Rao[1] showed that when carbon tetrachloride solutions of certain chlorine compounds of sulphur were treated with powdered potassium iodide, the unstable iodine analogues were produced. This paper deals with the reduction of these chlorine compounds by hydrogen iodide.

Experimental

Sulphur Chloride.—Sulphur chloride of C.P. quality was purified by the method of Harvey and Schuette[2] (*cf.*, Lowry, McHatton and Jones,[3] B. S. Rao,[4] M. R. A. Rao[1]). A stock solution of the chloride in pure carbon tetrachloride was prepared and the purity of the sulphur chloride was determined by analytical methods[5, 6] described by Rao. The ratio of sulphur to chlorine was found to be 1·0003.

Sulphur dichloride.—Sulphur dichloride (Kahlbaum's C.P. quality was purified by treatment with chlorine at 0° C., as suggested by Bothamley.[7] The purified dichloride was dissolved in carbon tetrachloride and the solution stored in a dark-coloured bottle and protected from moisture. Analytical determinations by methods indicated above showed that the ratio of chlorine to sulphur was 2·0004.

Thionyl chloride.—Purification was effected by fractional distillation of the chloride. A stock solution in carbon tetrachloride was prepared and the thionyl chloride was analysed by hydrolysis with dilute alkali (Schiff[8] and M. R. A. Rao[1]). As noticed by M. R. A. Rao,[1] a trace of sulphide was found in the products of hydrolysis. The ratio of chlorine to sulphur was 2.0005.

Sulphuryl chloride.—The carbon tetrachloride solution of sulphuryl chloride was prepared from a sample purified by fractional distillation. Purity was determined by the estimation of sulphate and chloride formed on

hydrolysis of the sulphuryl chloride by alkali. Ratio of chlorine to sulphur was 2·0002.

The reduction of the above chlorides by hydrogen iodide was carried out in dilute solutions by the technique described earlier.[9]

RESULTS

With all the four chlorides studied, there was immediate liberation of iodine, on treatment with hydrogen iodide. The iodine solutions in carbon tetrachloride however, did not at first have their normal violet colour, a yellowish tinge being imparted to the solution by the intermediate compound formed during the reaction. On keeping however, the characteristic iodine colour was finally obtained. The intermediate compound in each case was the iodine analogue of the chlorine compound used. When chlorine compounds were in very dilute solutions and the hydrogen iodide was relatively in large excess, the intermediate compound suffered further reduction and hydrogen sulphide was quantitatively formed. The ratio of hydrogen sulphide produced, to the iodine liberated, was in all cases approximately the number to be expected theoretically. The ratios of iodine to hydrogen sulphide obtained were 3·07 for sulphur chloride, 4·08 for sulphur dichloride, 6·06 for thionyl chloride and 8·02 for sulphuryl chloride.

The reactions taking place can be represented by the following equations:

I. $(S_2Cl_2 + 2HI \rightarrow S_2I_2 + 2HCl)$; $(S_2I_2 + 4HI \rightarrow 2H_2S + 6I)$.

$$S_2Cl_2 + 6HI \rightarrow 2H_2S + 6I + 2HCl \qquad (A)$$

II. $(SCl_2 + 2HI \rightarrow SI_2 + 2HCl)$; $(SI_2 + 2HI \rightarrow H_2S + 4I)$.

$$SCl_2 + 4HI \rightarrow H_2S + 4I + 2HCl \qquad (B)$$

III. $(SOCl_2 + 2HI \rightarrow SOI_2 + 2HCl)$; $(SOI_2 + 4HI \rightarrow H_2S + H_2O + 6I)$.

$$SOCl_2 + 6HI \rightarrow H_2S + 6I + H_2O + 2HCl \qquad (C)$$

IV. $(SO_2Cl_2 + 2HI \rightarrow SO_2I_2 + 2HCl)$; $(SO_2I_2 + 6HI \rightarrow H_2S + 2H_2O + 8I)$.

$$SO_2Cl_2 + 8HI \rightarrow H_2S + 8I + 2H_2O + 2HCl \qquad (D)$$

When the chlorine compounds employed were in moderately dilute solution, further reduction of the intermediate compound did not take place with sufficient rapidity to prevent its decomposition. Consequently, part of the sulphur appeared in the elemental condition in the final products. In the case of thionyl chloride and sulphuryl chloride, decomposition of the

intermediate compound yielded sulphur dioxide, part of which evidently suffered reduction by hydrogen iodide (*cf.*, Part II, present series[9]). The effect of concentration of the chloride solutions on the nature of the final products is evident from the results given in Table I.

Reaction Between Hydrogen Iodide and Chlorine Compounds of Sulphur

	Chloride	Expt. No.	Conc.* of chloride taken	% Chloride reduced to H_2S	% Chloride reduced to S	% Chloride reduced to SO_2
I	Sulphur monochloride	1	3·58	99·4	..	..
		2	7·32	99·2	..	..
		3	10·67	99·5	..	..
		4	76·25	49·1	50·7	..
		5	385·8	2·3	92·3	..
		6	412·6	2·3	90·2	..
II	Sulphur dichloride	1	4·27	98·6	..	..
		2	8·96	98·8	..	..
		3	12·36	99·4	..	..
		4	78·50	47·9	50·9	..
		5	93·46	45·8	53·3	..
		6	321·5	2·4	95·9	..
III	Thionyl chloride	1	6·35	99·1	..	..
		2	10·78	99·1	..	..
		3	15·57	99·4	..	..
		4	89·67	49·4	25·2	22·9
		5	112·5	46·8	26·3	25·5
		6	220·8	2·2	49·1	46·5
IV	Sulphuryl chloride	1	9·63	99·5	..	..
		2	10·48	98·9	..	..
		3	13·57	98·9	..	..
		4	18·63	99·4	..	..
		5	92·63	47·9	23·9	27·6
		6	108·5	47·2	20·5	29·9

* Quantities of sulphur and its compounds are expressed in terms of *g* atom of S $\times 10^6$ per g. of solution.

The formation of the intermediate compound and its subsequent decomposition could be confirmed in each case by spectrophotometric studies, using the Coleman Universal Spectrophotometer as described below.

A very dilute solution of each chloride was mixed in the dark with a moderately dilute solution of hydrogen iodide in carbon tetrachloride and transmittance measurement made. The measurements were repeated with

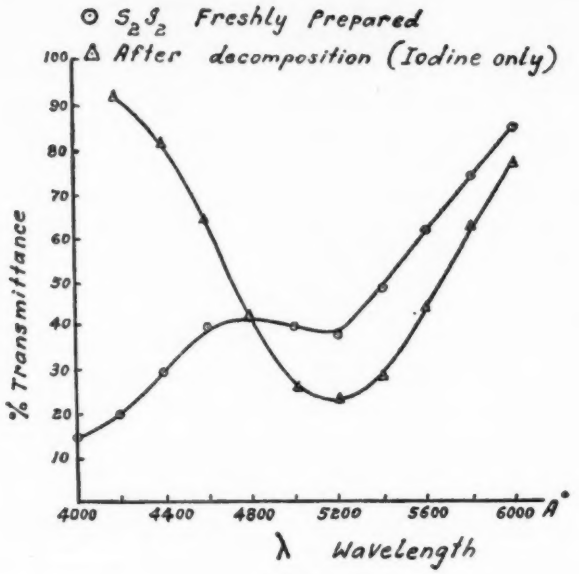
⊙ S_2I_2 Freshly Prepared
△ After decomposition (Iodine only)
% Transmittance
100
90
80
70
60
50
40
30
20
10
4000
4400
4800
5200
5600
6000 A°
λ Wavelength

FIG. 1

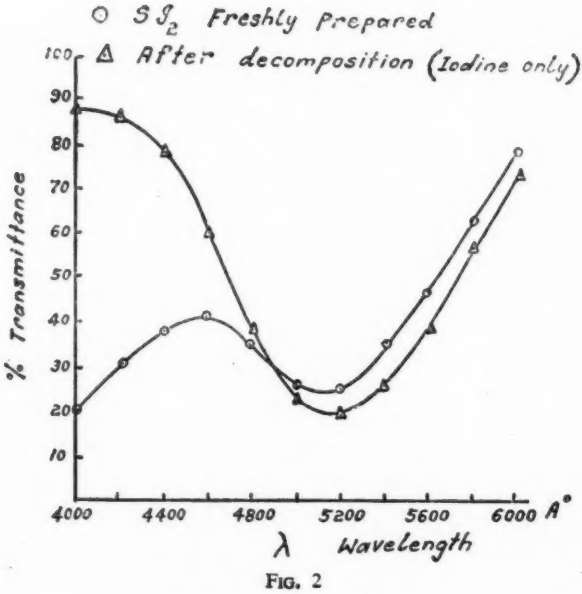
○ SI_2 Freshly Prepared
△ After decomposition (Iodine only)
% Transmittance
100
90
80
70
60
50
40
30
20
10
4000
4400
4800
5200
5600
6000 A°
λ Wavelength

FIG. 2

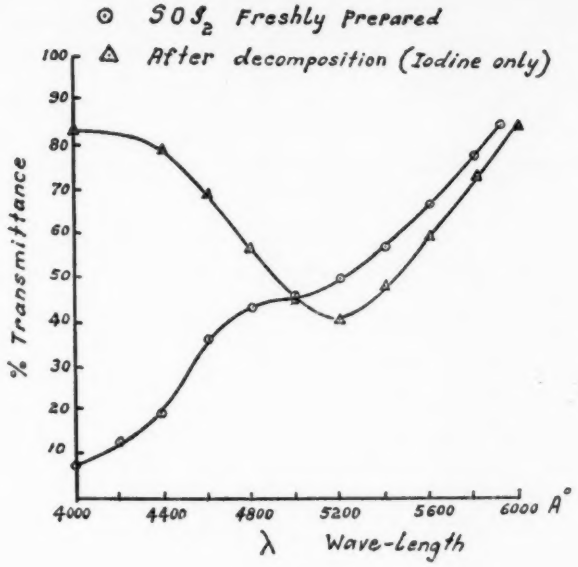

FIG. 3

the solution after it had been exposed to sunlight for 30 minutes to decompose completely the intermediate compound. The measurements were also made with standard solutions of iodine in carbon tetrachloride, to enable the estimation of iodine formed by decomposition. The results are presented graphically in Figs. 1, 2 and 3. When the solutions on mixing, were kept at a low temperature (— 16° C.) the decomposition, as was to be expected, was much lower. In the case of sulphuryl iodide a spectrophotometric study was not practicable owing to the highly unstable nature of this intermediate compound.

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STUDIES IN THE CHEMICAL BEHAVIOUR OF SOME COMPOUNDS OF SULPHUR

Part VI. The Reaction Between Hydrogen Iodide and Some Compounds of Sulphur

By A. R. Vasudeva Murthy

(*Indian Institute of Science, Bangalore*)

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It has been shown that hydrogen iodide is a valuable reagent in the study of the chemical behaviour of the oxides[1] and halides[2] of sulphur and of the esters of oxyacids[3] of the element. This paper deals with the reactions between hydrogen iodide and the following compounds of sulphur:—

Sulphur nitride, Hexasulphamide, Tetrahydrosulphur nitride ($H_4S_4N_4$), N-N tetraethyl-dithio-diamine, Tetra-ethyl-thio-diamine, Thionylaniline, Hydrogen disulphide and Hydrogen trisulphide.

(1) *Hydrogen Iodide and Sulphur Nitrides*

Sulphur Nitride.—Goehring[4] studied the reaction between sulphur nitride and a solution of potassium iodide in anhydrous formic acid and found that on addition of water, three atoms of iodine were liberated, per atom of nitrogen.

MacDiarmid[5] suggested that S_4N_3I was probably formed when hydrogen iodide reacted with sulphur nitride. The present author found that hydrogen sulphide was a significant product and the reaction was quantitatively studied by him.

Experimental

Sulphur nitride was prepared by passing dry ammonia into a chloroform solution of sulphur chloride as recommended by Arnold, Hugill and Hutson.[6] On purification, orange yellow needles of the nitride melting at 177° C. were obtained. A stock solution of sulphur nitride in carbon tetrachloride was prepared and the purity of the compound determined. Nitrogen was estimated by a modified Kjeldhal method using boric acid solution as an absorbent for ammonia and a mixed indicator (Bromcresol green and methyl red) in the titration.[7] Sulphur content was determined by hydrolysis of the nitride with alkali, followed by oxidation, and the estimation of the sulphate as its barium salt. The nitrogen content of the stock solution was $62{\cdot}82 \times 10^{-6}$ g. atoms of N per g. of solution while the sulphur value was $62{\cdot}88 \times 10^{-6}$ g. atoms, showing that the nitride was very pure.

Hexasulphamide.—This was obtained from the mother-liquor left on removal of sulphur nitride and purified by recrystallisation from alcohol, as suggested by Macbeth and Graham,[8] and Arnold, *et al.*[6] The crystals (square plates) of hexasulphamide melted at 108° C. The nitrogen content of the stock solution was $10{\cdot}81 \times 10^{-6}$ g. atoms of N per g. of solution and the sulphur value $65{\cdot}18 \times 10^{-6}$ g. atom. The ratio of S to N was thus 6·03, the theoretical value being 6·00.

Tetrahydro Sulphur Nitride.—Sulphur nitride solution in benzene was reduced by stannous chloride in alcoholic solution, as recommended by Meuwsen,[9] to obtain tetrahydro sulphur nitride. The compound was purified by recrystallisation.

Reaction with Hydrogen Iodide.—Dilute solutions of the above three sulphur compounds were introduced into bulbs containing dry hydrogen iodide. The liberated iodine and hydrogen sulphide were estimated in the usual way. After titrating the iodine, the aqueous layer was employed for the determination of ammonia by the Kjeldahl method. The results are presented in the following table (Table I).

TABLE I

Reaction Between Hydrogen Iodide and Certain Nitrogen Compounds of Sulphur

Compound	Expt. No.	Nitride taken*	Hydrogen sulphide obtained	Iodine g. atom × 10^6 per g. of solution	Ammonia as g. of N × 10^6 per g. of solution	Ratio $I : H_2S$	Ratio $NH_3 : H_2S$
Sulphur Nitride (N_4S_4)	1	4·83	4·80	24·12	4·87	5·01	1·01
	2	7·28	7·16	35·96	7·18	5·02	1·00
	3	10·54	10·48	52·64	10·52	5·02	1·00
	4	15·65	15·54	78·58	15·58	5·02	1·00
					Ave.	5·02	1·00
Hexasulphamide (S_6NH_2)	1	6·84	6·78	14·98	1·12	2·21	0·165
	2	8·98	8·86	19·65	1·45	2·22	0·164
	3	12·24	12·15	26·92	2·02	2·21	0·166
	4	15·66	15·56	34·05	2·58	2·18	0·166
					Ave.	2·20	0·165
Tetrahydro sulphur nitride ($H_4N_4S_4$)	1	5·53	5·49	22·08	5·51	4·02	1·00
	2	7·62	7·56	30·31	7·58	4·01	1·00
	3	13·48	13·34	53·63	13·38	4·02	1·00
	4	17·76	17·68	71·25	17·72	4·03	1·00
					Ave.	4·02	1·00

* Quantities of sulphur and its compounds have been expressed in terms of g. atoms of S × 10^6 per g. of solution.

The experimental results indicate that the reduction of the nitrogen compounds of sulphur proceeds as follows:

$$N_4S_4 + 24\,HI \rightarrow 4\,H_2S + 4\,NH_4I + 20\,I \quad (1)$$

$$S_6NH_3 + 14\,HI \rightarrow 6\,H_2S + NH_4I + 13\,I \quad (2)$$

$$H_4S_4N_4 + 20\,HI \rightarrow 4\,H_2S + 4\,NH_4I + 16\,I \quad (3)$$

It will be noticed from the above equations that a molecule of each of the nitrogen compounds reacts with a large number of molecules of hydrogen iodide. Undoubtedly the above reactions take place in several stages. Intermediate stages in the reduction of sulphur compounds by hydrogen iodide have been noticed in several cases.[1, 2, 3] With the above nitrogen compounds, however, it was not practicable to prove experimentally the formation of intermediate compounds as the reduction with hydrogen iodide proceeded rapidly to the final stage of hydrogen sulphide.

The nature of the reaction between hydrogen iodide and sulphur nitride (and its tetrahydro derivative) has been interpreted by Goehring[4] as evidence of the oxidising power of sulphoxylic acid (H_2SO_2), under certain conditions.[10] To explain the results, it is however hardly necessary to ascribe oxidising power to sulphoxylic acid. It is well known that in non-aqueous media, hydrogen iodide is an energetic reducing agent. The observation of Goehring can be satisfactorily explained on the basis of this powerful reducing action of hydrogen iodide.

As has already been pointed out,[1] Goehring added water to the formic acid solution of potassium iodide on its reaction with the sulphur compounds studied. Thereby, the true nature of the reaction was masked as the hydrogen sulphide liberated was oxidised by iodine. If this oxidation of hydrogen sulphide is taken into account, we find that the experimental results of Goehring are in agreement with the findings of the present author. Goehring found that per atom of nitrogen in sulphur nitride, three atoms of iodine were liberated, while the present author found that 5 atoms of iodine and a molecule of hydrogen sulphide were set free for every atom of nitrogen, as indicated in equation (1).

(2) *Hydrogen Iodide and Thioamines*

Stamm and Goehring[10, 11] reported the liberation of iodine when tetramethyl-dithio-diamine and tetraethyl-thio-diamine were treated with formic acid solutions of potassium iodide. The action of hydrogen iodide on the two thioamines and on thionyl aniline has been studied quantitatively by the present author, using the technique described in an earlier paper.

Tetraethyl-dithio-diamine and tetra-ethyl-thio-diamine were prepared by treating diethyl amine with calculated amounts of disulphur dichloride and sulphur dichloride respectively, in petroleum-ether solution (Lengfeld and Stieglitz[12] and Michaelis and Luxembourg[13]). Thionyl aniline was prepared by treating aniline with a suitable quantity of thionyl chloride in benzene (Michaelis and Herz[14]). The three liquids were purified by distillation under reduced pressure. Stock solutions of the thioamines in carbon tetrachloride were prepared and the solutions analysed for their nitrogen and sulphur contents. The ratio of N to S was 1·005 for tetraethyl-dithio-diamine, 2·008 for tetraethyl-thio-diamine and 1·003 for thionyl aniline.

Reaction with Hydrogen Iodide.—Dilute solutions of the compounds were introduced into bulbs containing hydrogen iodide.[1] The solution first acquired a reddish yellow tinge which finally changed to the characteristic purple of iodine (*cf.* Part II of this series). The iodine and hydrogen sulphide produced were estimated in the usual way. The experimental data are given in Table II.

TABLE II

Reaction between Hydrogen Iodide and Thioamines

Compound	Sl. No.	Thioamine used*	H_2S produced	Iodine liberated in g. atoms $\times 10^6$ per g. of solution	Ratio L : H_2S
Tetraethyl-dithio-diamine $S_2(NEt_2)_2$	1	8·76	8·68	26·17	3·02
	2	11·84	11·75	35·37	3·01
	3	15·32	15·26	46·16	3·03
	4	19·56	19·48	58·65	3·01
Tetraethyl-thio-diamine $S(NEt_2)_2$	1	7·58	7·48	30·30	4·05
	2	12·46	12·36	49·68	4·02
	3	17·25	17·18	69·23	4·03
	4	22·85	22·78	91·33	4·01
Thionyl aniline C_6H_5NSO	1	8·78	8·69	52·31	6·02
	2	15·36	15·28	92·11	6·03
	3	22·25	22·12	132·9	6·01
	4	28·64	28·58	172·3	6·03

* Quantities of sulphur and its compounds are expressed in terms of g. atoms of S $\times 10^6$ per g. of solution.

The results indicate that the reduction of the above compounds follows the equations:

$$S_2(NEt_2)_2 + 8\,HI \rightarrow 2\,H_2S + 2\,NHEt_2.HI + 6\,I \quad (4)$$

$$S(NEt_2)_2 + 6\,HI \rightarrow H_2S + 2\,NHEt_2.HI + 4\,I \quad (5)$$

$$C_6H_5NSO + 7\,HI \rightarrow H_2S + C_6H_5NH_2.HI + H_2O + 6\,I \quad (6)$$

(3) *Hydrogen Iodide and Hydrogen Persulphides*

Dihydrogen disulphide and dihydrogen trisulphide in carbon tetrachloride solution were found to liberate iodine on treatment with hydrogen iodide. A quantitative study of the reaction is given below.

Purified samples of dihydrogen disulphide and dihydrogen trisulphide were prepared by the distillation under reduced pressure of crude polysulphide oil (Walton and Parsons[15]). Stock solutions of the sulphides in dry carbon tetrachloride were prepared and analysed in the following way.

A known weight of the stock solution was shaken with about 5 g. of pure mercury in an all-glass apparatus. The hydrogen sulphide evolved was swept off in a current of dry nitrogen and estimated iodometrically. The mercury sulphide formed was determined by the method of B. S. Rao and M. R. A. Rao.[16] The ratio of HgS to H_2S was 1·005 for the disulphide and 2·008 for the trisulphide.

The above analytical method was found to be more accurate than the procedure described by Feher, Talpay and Heuer,[17] who decomposed the persulphide catalytically on glasswool and estimated the hydrogen sulphide argentimetrically and weighed the sulphur liberated.

Reaction with Hydrogen Iodide.—Known amounts of solutions of the persulphides were introduced into bulbs containing hydrogen iodide. The iodine, hydrogen sulphide and elemental sulphur (if any) produced in the reaction were estimated by methods described earlier. The data are given in Table III.

TABLE III

Reaction Between Hydrogen Iodide and Hydrogen Persulphide

Compound	Expt. No.	Persulphide taken*	H_2S obtained	Iodine in g. atom $\times 10^6$ per g. of soln.	Ratio I : H_2S
Hydrogen disulphide	1	6·86	6·78	6·92	1·02
	2	11·54	11·46	11·81	1·03
	3	16·32	16·12	16·28	1·01
	4	22·65	22·48	22·92	1·02
Hydrogen trisulphide	1	5·95	5·84	7·82	1·34
	2	12·76	12·58	16·98	1·35
	3	18·28	18·12	24·11	1·33
	4	22·34	22·16	29·7	1·34

* Quantities of sulphur and its compounds have been expressed in terms of g. atoms of S $\times 10^6$ per g. of solution.

From the above results it may be concluded that the concerned reactions are:

$$H_2S_2 + 2\,HI \rightarrow 2\,H_2S + 2\,I \text{ (Ratio of I to } H_2S\ 1{\cdot}0) \quad (7)$$

$$H_2S_3 + 4\,HI \rightarrow 3\,H_2S + 4\,I \text{ (Ratio of I to } H_2S\ 1{\cdot}33) \quad (8)$$

The actual ratio of iodine to hydrogen sulphide was slightly more than unity for the disulphide. This was probably due to a small quantity of the trisulphide present as impurity. Known quantities of sulphur in carbon tetrachloride solution were added to solutions of the disulphide and the trisulphide, before treatment with hydrogen iodide. It was found that the dissolved sulphur, even in presence of persulphide, did not liberate any iodine from hydrogen iodide (*cf.* Part II of this series). There was thus no activation of the dissolved sulphur by the persulphide.

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QUANTITATIVE DETERMINATION OF COPPER, CUPROUS OXIDE AND CUPRIC OXIDE IN A MIXTURE*

By S. M. Mehta, F.A.Sc. and N. R. Bharucha

(The Department of Chemistry, The Institute of Science, Bombay)

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It is well known that the selective dissolution of cuprous oxide from its mixture with metallic copper and cupric oxide is difficult and militates against the evolution of a simple and accurate method for the quantitative analysis of the mixture.

Le Blanc and Sachse[1] determined cupric oxide iodometrically in a mixture of cuprous oxide and cupric oxide. Action of iodine on the metallic copper present affects, however, the accuracy of the method.

Bonner and Kaura[2] suggested the extraction of the two oxides with a solution of sodium cyanide. Hurd and Clark[3] pointed out that finely divided copper was attacked by the reagent and that the dissolution losses varied directly with the amount of cupric oxide in the sample and the volume of the reagent employed.

Fitzpatrick[4] attempted the separation of metallic copper by boiling the mixture with a saturated silver sulphate solution. Even during the few minutes of extraction, a considerable amount of cuprous oxide reacted to form metallic copper and gave high copper values (*cf.* Hurd and Clark, *loc. cit.*).

Zerfoss and Willard[5] estimated the three components microscopically, after treating the sample with dilute HCl. The method was however unsuitable as it involved rapid counting of the particles to eliminate errors due to the action of dilute HCl on the cupric oxide. Furthermore, the method was tedious.

Mitchell, Smith, Ashby, and Bryant[6] used the Karl Fischer reagent. This dissolved Cu_2O readily but had practically no effect on cupric oxide and could be employed for the estimation of the two oxides in a mixture. The authors, however, do not seem to have examined the use of this reagent

* This method was developed in connection with an investigation on the corrosion of brass by alkalis.

for the estimation of cuprous oxide, cupric oxide and metallic copper, in a mixture.

Hurd and Clark[3] described a method based on the extraction of cuprous oxide by cold aqueous ammonia, containing hydrazine sulphate (to inhibit dissolution of cupric oxide). The absorption of carbon dioxide by the aqueous ammonia affected accuracy as pointed out by Baker and Gibbs.[7] The present authors found that in spite of precautions, a small quantity of CuO invariably dissolved and gave erroneous results by this method.

For the extraction of Cu_2O, Baker and Gibbs[7] suggested aqueous HCl (dilute) but later preferred an alcoholic solution.[8] The present authors find that even alcoholic HCl has marked solvent action on CuO.

Drawe[9] attempted analytical separation of the oxides using dilute sulphuric acid (1 : 5) to dissolve CuO. The cuprous oxide reacted with the acid to give copper and copper sulphate, but the metal liberated could be estimated and a correction applied. The solvent action of the acid on the finely divided copper introduced an error.

Nishida and Hirabayashi[10] claimed that copper was practically insoluble in dilute sulphuric acid (3 to 6 N) at room temperature during the 20 minutes required to dissolve cupric oxide completely. Any cuprous oxide present, would completely dissolve in the reagent and yield a solution that quantitatively reacted with permanganate. As observed by Drawe, however, cuprous oxide while reacting with sulphuric acid liberated some metallic copper which adversely affected the results.

Recently, Lavrukhina[11] has described a method for the determination of Cu, Cu_2O and CuO when present in a mixture. According to the method, which is carried out with a special apparatus, the weighed quantity of the mixture is treated with 15 c.c.'s of a solution containing 9 parts of 1.2 N HCl, 3 parts of 3% hydrazine sulphate and 3 parts of 10% KCl in an atmosphere of CO_2 and the Cu_2O dissolved out and collected in the filtrate is titrated with $Ce(SO_4)_2$ at 70°–80° C. The residue which now consists of a mixture of CuO and Cu is treated with a solution containing $FeCl_3$ and HCl so as to dissolve metallic Cu, which is estimated in the filtrate potentiometrically as before. Finally the CuO is dissolved in hot 20% HCl and the solution treated with hydrazine sulphate and NaCl and Cu estimated as before. It may be pointed out, however, that the acidified $FeCl_3$ solution will dissolve CuO and is likely to cause an error.

In the following paragraphs, therefore, a new method has been described. It is found to give very satisfactory results.

Experimental

The Cu_2O used was an electrolytic product of 99·8% purity obtained by the anodic oxidation of copper in an alkaline solution.[12] The CuO was of "Extra Pure" quality from E. Merck. Both were sieved through 200 mesh. The copper used in the experiments was metal powder from E. de Haen works. It was purified by boiling with a saturated solution of KI, washing with water, alcohol and ether and finally drying in a vacuum desiccator.

Extraction Solution.—Hot saturated solution of KI.

Ferric Chloride Solution.—$FeCl_3 6H_2O$ (150 g.) and HCl (1·2 sp. gr.) 300 c.c. made up to 800 c.c. with air free, CO_2 saturated, distilled water.

Indicator.—Diphenylamine sulphonate indicator was prepared by treatment of the barium salt with sodium sulphate, decanting off the supernatant liquid and preserving in a dark coloured bottle.

Phosphoric Acid.—85% solution of ortho-phosphoric acid of Reagent quality.

Potassium Dichromate.—0·1N solution of A.R. potassium dichromate.

Procedure.—Synthetic mixtures were prepared by weighing different amounts of metallic copper, cuprous oxide and cupric oxide, and mixing thoroughly. Each sample of the mixture was then divided into three equal parts for individual determinations of (*a*) metallic copper, (*b*) Cu_2O, and (*c*) total copper.

1. The weighed sample was treated with hot saturated solution of KI for about five minutes, with frequent stirring, so as to dissolve the Cu_2O present. At the end of this period, the solution together with the unaffected Cu and CuO was quickly transferred to a filter-paper and the solution allowed to drain off completely. The residue on the filter-paper was then washed first with small amounts of distilled water containing CO_2, until all the extraction solution, containing dissolved Cu_2O, was removed. The residue now containing Cu and CuO was next dissolved in about 30 c.c. of ferric chloride solution by stirring and gentle heating on a steam-bath. The solution was allowed to cool, made to a known volume and then titrated with standard $K_2Cr_2O_7$ using 15 c.c. of phosphoric acid and three drops of the indicator.

2. For the estimation of Cu_2O, the weighed sample was dissolved directly in ferric chloride solution, made to a known volume, and titrated with standard $K_2Cr_2O_7$ exactly as stated above. The cuprous oxide content was calculated from the difference in the two titre values.

3. In order to estimate the amount of CuO in the mixture, the weighed sample was dissolved in the minimum quantity of concentrated HNO_3. The solution thus obtained was treated with urea and boiled for a few minutes in order to remove any oxides of nitrogen present. The resulting solution was cooled and made to 250 c.c. The copper content of this solution was determined iodometrically. Knowing the total copper, elemental copper, and cuprous oxide, the cupric oxide content was calculated.

Results of the Analysis.—The method outlined here was applied to different artificial mixtures of copper, cupric oxide and cuprous oxide. Data obtained are tabulated below.

Mixture of $Cu + Cu_2O + CuO$

Cu (in g.)		Cu_2O (in g.)		CuO (in g.)	
Taken	Estimated	Taken	Estimated	Taken	Estimated
0·5571	0·5569	0·7304	0·7305	0·3975	0·3977
0·2254	0·2251	0·2331	0·2333	0·2593	0·2595
0·4068	0·4064	0·4806	0·4809	0·6951	0·6950
0·8752	0·8750	0·4369	0·4368	0·6072	0·6074
0·0826	0·0825	0·9718	0·9716	0·9716	0·9712

SUMMARY

Advantage is taken of the solubility of cuprous oxide in hot saturated solution of potassium iodide in which metallic copper and cupric oxide are insoluble. The residual mixture of metallic copper and cupric oxide is then treated with acidified ferric chloride and the ferrous iron corresponding to the metallic copper titrated with dichromate or ceric sulphate.

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STUDIES IN IRON OXIDE SOLS

Part II. Membrane Equilibrium in Iron Oxide Sol

By A. K. M. Trivedi and A. S. Divatia

(L. D. Arts College and M. G. Science Institute, Ahmedabad)

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If a colloid like iron oxide sol is kept in a collodion bag and is allowed to come to an equilibrium with the diffusate outside the bag, then, there will be an unequal distribution of free electrolyte like hydrochloric acid across the membrane due to the following reasons:—The amount of free hydrogen ion per unit volume will be less within the bag than that without the bag, due to (*a*) the establishment of Donnan Membrane equilibrium effect (Donnan[1]) and (*b*) the volume occupied by the colloidal micelles (Fe_2O_3 plus the water of hydration). On the other hand, adsorption of the hydrogen ions by the micelles will lead to the increase of the free hydrogen ions inside the bag as compared to that outside. In the case of iron oxide sol of Graham type, as in sulphur sol, the free hydrogen ions are not likely to be adsorbed (Bolam and Trivedi[2]). If the composition of the sol is determined and if further it is assumed that ten per cent. of the fixed hydrogen ions contribute to the membrane equilibrium effect, it will be possible to determine the extent of hydration in iron oxide sol (see discussion). Iron oxide sols are known to be hydrated (Freundlich[3]) but as far as we are aware few, if any, attempts have been made to estimate the extent of hydration.

Experimental

In the present work, partially dialysed sols of Graham type were kept in collodion bags, suspended in water for three weeks until equilibrium was undoubtedly established. Care was taken to avoid evaporation and to protect the sol from light. The apparatus was kept at room temperature. Some difficulty was experienced in obtaining collodion prepared in a mixture of alcohol and ether. Most of the samples available in the market are prepared in methylated spirit instead of ethyl alcohol, and the bags obtained from such a sample of collodion were impermeable. Ultimately collodion prepared by Mallinckrodt Co. (U.S.A.) was obtained. The collodion bags were prepared by coating internal surface of pyrex glass tubes $1'' \times 8''$ in

a manner described by Hatschek.[4] Although the liquid was allowed to drain off very slowly from the test tube, so as to give an almost uniformly thick-walled bag, it was not possible to obtain a membrane which retained the whole of the iron oxide sol. However, the concentration of the colloid inside the bag was always much greater than that outside the bag. No attempt was made to measure the osmotic pressure that was developed. When equilibrium was attained, the sols inside and outside the bag were analysed for free hydrogen-ion concentration, bound hydrogen-ion concentration and the iron oxide content. For the purpose in view, the most important measurement was the determination of the free hydrogen-ion concentration inside and outside the bag. Hence, 25 ml. of the sol inside and outside the bag, were taken for the determination of the free hydrogen-ion concentration and 10 ml. of the sol inside and outside the bag, for the determination of the iron oxide content. The method of preparation of the sol and methods of chemical analysis have been given in a previous paper (" Studies in Iron Oxide Sols, I, Vol. 36, p. 530). In this case, however, as the quantity of the sol was limited, the coagulum obtained by addition of sodium sulphate tothe sol, was utilised for the determination of the fixed hydrogen-ion concentration. In Table I are given the data obtained in different experiments. The values in gm./1. (Fe_2O_3) are obtained on multiplying the corresponding values of 10 ml. by 100, and the values of hydrogen-ion concentration, both fixed and free, in m.e./1. are obtained on multiplying the corresponding values by two. Hence a separate table is not given for the above quantities.

TABLE I

Sol No.	Gm. of iron oxide in 10 ml. of sol		Ml. of N/20 NaOH required by 25 ml. of sol for free H		Ml. of N/20 NaOH required by 25 ml. of sol for fixed H	
	"I"	"O"	"I"	"O"	"I"	"O"
1	0·269	0·008	5·7	7·0	3·1	0·3
2	0·241	0·004	6·4	8·7	5·0	0·2
3	0·253	0·009	6·7	8·4	5·9	0·5
4	0·251	0·019	6·9	8·7	6·5	0·4
5	0·258	0·012	7·3	9·0	4·7	0·3
6	0·263	0·006	6·9	9·4	3·3	0·2
7	0·248	0·013	7·3	9·2	6·6	0·3
8	0·240	0·008	6·4	7·9	4·0	0·3
9	0·242	0·014	6·5	8·1	4·2	0·3
10	0·261	0·004	6·7	9·1	4·6	0·3

Discussion

It is easy to see that the free hydrogen-ion concentration outside the membrane is considerably greater than that inside the membrane and that the difference in the free hydrogen-ion concentration is far beyond the experimental error. It may, therefore, be assumed that these differences are real and are due to (*a*) the membrane equilibrium effect and (*b*) the hydration effect, as the adsorption of the free hydrogen ions is not possible. If it is further assumed that only ten per cent. of the bound ions contribute to the membrane equilibrium effect (McBain and Thomas[5]), then the hydration of the micelles can be calculated in the following way:—According to Donnan's fundamental relation (T. R. Bolam[6]), and assuming that the activities of the chloride and the hydrogen ions are identical with their relatively low concentrations, we have:

$$(H_B)_I = \frac{[(H_F)_O]^2 - [(H_F)_I]^2}{[(H_F)_I]} \qquad (1)$$

where $(H_B)_I$ = concentration of bound hydrogen ions inside the bag $(H_F)_I$ = the concentration of free hydrogen ions inside the bag and $(H_F)_O$ = the concentration of free hydrogen ions outside the bag; all concentrations are expressed in m.e./l.

As only ten per cent. of the bound hydrogen ions are effective in membrane equilibrium, we can calculate "x", *i.e.*, the concentration of free hydrogen ions outside the bag [the hypothetical value of $(H_F)_O$, if the difference between $(H_F)_O$ and $(H_F)_I$ is only due to the membrane equilibrium effect]. For calculations, the difference between $(H_B)_I$ and $(H_B)_O$ is used instead of $(H_B)_I$. In practice it was found that $(H_F)_O$ was always higher than "x". The volume "V" occupied by the micelles, the apparent density "D" of the micelles and the specific hydrodynamic volume can be calculated by the equations similar to the equations given in the case of sulphur sol (Bolam and Trivedi[2]) and arsenic sulphide sol (Trivedi and Patani: Paper submitted to the *J.I.C.S.*):

$$D = \frac{[(H_F)_O] \times [(Fe_2O_3)_I - (Fe_2O_3)_O]}{1000\,[(H_F)_O - "x"]} \qquad (2)$$

The value of density D comes out to be much lower than the density of iron oxide (Mellor[7]). S. H. V. is the ratio of the actual and the apparent density of iron oxide. In Table II are given the calculated values of "x", the observed values of $(H_F)_O$, the apparent densities and the values of S.H.V. for different experiments.

TABLE II

Sol No.	Calculated value of "x" m.e./l.	Observed value of $(H_r)_o$ m.e./l.	Apparent density "D"	S.H.V.
1	11·7	14·0	0·159	30·93
2	13·3	17·4	0·101	48·87
3	13·9	16·8	0·141	34·85
4	14·4	17·4	0·135	36·40
5	15·0	18·0	0·148	33·29
6	14·1	18·8	0·103	47·79
7	15·2	18·4	0·135	36·40
8	13·2	15·8	0·141	34·85
9	13·4	16·2	0·132	37·26
10	13·8	18·2	0·106	46·23

It is easily seen that in all cases, the apparent density " D " is much lower than the actual density of iron oxide (4·913) and the values of S.H.V. are always greater than one. It therefore follows that the micelles contained water which is not acting as a solvent for hydrogen-ions. The average of S.H.V. is about 40 (it must be admitted that the figure obtained is liable to some error). Thus there are 39 ml. of non-solvent water to one ml. of iron oxide, or 39 gm. of water to 4·913 gm. of Fe_2O_3 :—

There are $(39/18) \times (1000/4{\cdot}913) = 441$ millimoles of water to one gram of Fe_2O_3. Multiplying this by the molecular weight (160) of iron oxide:

$(160) \times (441/1000) = 70{\cdot}56$. Thus there are about 70 moles of water to one mol of iron oxide in the micelles.

Thus the micelles in the case of iron oxide sol are highly hydrated; the hydration in the case of iron oxide sol being much greater than that in the case of sulphur sol (Bolam and Trivedi[2]) or arsenic sulphide sol (Trivedi and Patani[8]). In Table III are given the millimoles of water per gram of colloid.

TABLE III

Name of the colloid	Millimoles of water/gm. of colloid
Sulphur	30·00
Arsenic sulphide	14·33
Iron oxide	441·00

The micelles in the case of iron oxide sol are highly hydrated, has been assumed by nearly all workers, and is borne out by the present investigation.

Summary

The unequal distribution of an electrolyte across a semipermeable membrane, in the presence of iron oxide sol is partly due to the establishment of (*a*) the membrane equilibrium and (*b*) hydration of micelles. Assuming that ten per cent. of the bound hydrogen ions are active in membrane equilibrium the hydration in the case of iron oxide micelles is calculated. It has been found that there are about 441 millimoles of water to one gram of iron oxide.

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THE PREPARATION OF THE DOUBLE SULPHATES OF TIN AND CERTAIN BIVALENT METALS

By S. R. Patel

(The Department of Chemistry, The Institute of Science, Bombay)

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This paper deals with the preparation of the compounds of the type $RSO_4.Sn(SO_4)_2$, where R = zinc, cobalt, magnesium, manganese and cadmium. Of the combinations of the sulphate of tetravalent tin with the sulphates of bivalent metals, the only ones described in literature are combinations with the sulphates of calcium, barium, strontium and lead.[1]

A stock solution of stannic sulphate was prepared by heating stannous chloride in conc. sulphuric acid to white fumes. 10 c.c. of this solution corresponded to 0·060 g. of SnO_2. In each experiment, 20 c.c. of this solution were diluted to 50 c.c. with conc. sulphuric acid and then heated in presence of bivalent metallic sulphates. From the clear solution first obtained, a precipitate separated out on further heating. The precipitate was filtered through a sintered glass crucible (Jena, 1G4) and washed thrice with conc. sulphuric acid and then with absolute alcohol to remove sulphuric acid. It was dried at 220–30° C., dissolved in hydrochloric acid, and analysed as follows:

Zinc, magnesium and cobalt were separated from tin by precipitating the latter as hydroxide with ammonia and ammonium chloride. The hydroxide was dissolved in hydrochloric acid and reprecipitated. This step was repeated and the three filtrates obtained were mixed together. From this solution zinc, cobalt or magnesium was estimated as oxinate while tin was determined directly by the cupferron method. Manganese and tin in the manganese compound were estimated directly by the bismuthate and the cupferron methods respectively. In the case of the cadmium salt, the cadmium was precipitated as sulphide in the presence of sodium hydroxide and was weighed as cadmium sulphate. From the filtrate, tin was estimated by the cupferron method. Sulphate was determined as barium sulphate.

The results obtained are reported in Table I.

TABLE I

Bivalent sulphate	Wt. of bivalent sulphate in g.	% of tin	% of bivalent metal	% of sulphate	Formula
$ZnSO_4.7H_2O$	0·120	25·2	14·1	61·2	
	0·240	24·8	13·5	60·8	$ZnSO_4.Sn(SO_4)_2$
	0·480	24·7	14·2	61·1	
$CoSO_4.7H_2O$	0·120	25·9	12·3	61·6	
	0·240	25·1	12·7	62·3	$CoSO_4.Sn(SO_4)_2$
	0·480	25·7	12·1	62·4	
$MgSO_4.7H_2O$	0·120	27·2	4·9	66·6	
	0·240	27·1	5·1	67·1	$MgSO_4.Sn(SO_4)_2$
	0·480	26·9	5·3	66·9	
$MnSO_4$ (anhydrous) ..	0·120	25·6	11·3	62·7	
	0·240	25·4	11·4	62·2	$MnSO_4.Sn(SO_4)_2$
	0·480	25·9	12·1	62·1	
$CdSO_4$ (anhydrous) ..	0·120	23·1	21·9	55·7	
	0·240	22·8	21·7	55·2	$CdSO_4.Sn(SO_4)_2$
	0·480	22·5	21·5	55·5	

The compounds $RSO_4.Sn(SO_4)_2$ are all hygroscopic and are hydrolysed by water. The cobalt compound is pink, the manganese salt light yellow while the other three compounds are white. An optimum yield of these compounds (50 to 60%) is obtained when 0·48 g. of the bivalent sulphate is used.

A comparative study was made of electrical conductivities of solutions of these compounds on hydrolysis and of artificial solutions prepared on the assumption that each molecule of $RSO_4.Sn(SO_4)_2$ liberated on hydrolysis two molecules of sulphuric acid and one molecule of bivalent metallic sulphate.

The measurements showed that the conductivity for the solutions obtained from the compound $RSO_4 . Sn(SO_4)_2$ and for similar solutions prepared artificially, were very close to each other indicating that these compounds are double sulphates.

SUMMARY

The compounds $RSO_4 . Sn(SO_4)_2$ have been prepared. Conductivity measurements of the solutions obtained from $RSO_4 . Sn(SO_4)_2$ when compared with those of similar solutions prepared artificially show that the substances are double sulphates.

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THEORY OF IMAGE FORMATION IN COMBINATIONS OF X-RAY FOCUSSING MIRRORS

By Y. T. Thathachari

(*Department of Physics, Indian Institute of Science, Bangalore-3*)

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1. Introduction

It is possible to form magnified X-ray images of objects by illuminating them with white X-rays and obtaining Laue reflections from the lattice planes of crystals bent into an approximately spherical surface (Ramachandran and Thathachari, 1951). The paraxial theory of the combinations of spherical crystalline reflectors forming X-ray microscopes has been recently worked out (Thathachari and Ramachandran, 1952). The purpose of the present paper is (1) to deduce analytically the possible combinations of X-ray focussing mirrors which will give rise to an X-ray image and (2) to develop the geometrical optical theory of such combinations for aperture radii and distances of the object points from the axis, whose fourth and higher powers can be neglected in comparison with the corresponding powers of the radii of curvature of the mirrors. The matrix notation originally suggested by Smith (1945, 1948), and Herzberger (1943) and recently improved upon by Clyde Harris (1950) is used throughout the paper with suitable modification and improvement wherever necessary.

2. A Brief Account of the Matrix Method in Ray-Tracing

Any ray in an optical system can be completely specified by two parameters, one defining its position and the other its direction. Let them be denoted by **A** and **b** respectively. During the passage through the system, each ray undergoes two types of changes, *viz.*, (1) a bodily displacement due to transit from one surface to the next and (2) a change in its direction brought about by reflection at the surface. We shall refer to the two changes as interval and reflection transformations respectively. If unaccented and accented magnitudes refer respectively to conditions before and after any one of these changes, an interval transformation has the form

$$\mathbf{A}' = \mathbf{F}_1(\mathbf{A}, \mathbf{b})$$

and

$$\mathbf{b}' = \mathbf{b}$$

and a reflection transformation has the form

$$\mathbf{A}' = \mathbf{A}$$

and

$$\mathbf{b}' = \mathrm{F}_2(\mathbf{A}, \mathbf{b}),$$

where F_1, F_2 refer to functions of **A** and **b** and can be determined in the former case from the nature of the two surfaces and their mutual orientation and in the latter, from the law of reflection and the shape of the reflecting surface. Different meanings can be attached to the parameters **A** and **b**.

Let the optical axis of the system be defined by the unit vector **K**. The reference planes (*e.g.*, the planes containing the object and the image points and those tangential to the reflecting surfaces at their vertices) are all supposed to be orthogonal to the optic axis. We can define the position of a ray by the vector **a** drawn from the intersection of a reference plane with the axis to its intersection with the ray, *i.e.*, the vector intercept of the ray on the reference plane. The direction of the ray can be defined by its slope **b**. It is found convenient, however, to choose $\mathbf{A} = \rho\mathbf{b}$ as the position defining parameter, where ρ is the curvature of the corresponding reflecting surface at its vertex. Then **A** can be taken to be a measure of the aperture of the reflector. Similarly it is convenient to choose as the direction parameter the vector **b** along the projection of the ray in the same reference plane and of magnitude equal to its slope b. Thus a ray is completely specified if the vectors **A**, **b** are known in any of the reference planes.

When the ray proceeds from one surface to the next, we have, by the definition of **b**,

$$\mathbf{a}' = \mathbf{a} + \mathbf{b}z$$

and

$$\mathbf{b}' = \mathbf{b},$$

where z is the separation between the reference planes and is positive or negative according as the transit is in the positive or negative direction of **K**. We shall define the positive direction of **K** as that from the vertex to the centre of curvature of the reflecting surface, during the reflection at that surface and the subsequent displacement of the ray to the next surface. Thus, if the ray encounters a second surface for which the direction from the vertex to the centre is opposite to that of the first, then the sign of the unit vector **K** must be reversed for the subsequent transformations. Hence, for an interval transformation

$$\mathbf{A}' = \mathbf{A} + \mathbf{b}Z$$

and

$$\mathbf{b}' = \mathbf{b}$$

where $\dot{Z}$ is written for $z\rho$. In matrix notation

$$(\mathbf{A}', \mathbf{b}') = (\mathbf{A}, \mathbf{b}) \begin{pmatrix} 1 & 0 \\ Z & 1 \end{pmatrix}. \tag{1}$$

This matrix which transforms $(\mathbf{A}, \mathbf{b})$ into $(\mathbf{A}', \mathbf{b}')$ after a displacement of the ray may be described as the interval matrix $\mathbf{I}(Z)$. The corresponding matrix in the case of reflection may be called the reflection matrix R.

The passage of a ray through the system can be completely described by events which are alternately of the two types, *viz.*, (1) displacement and (2) reflection. Since in each case the new values of the ray-defining parameters can be obtained in terms of those prior to the change by the corresponding matrix of transformation, it is obvious that the values of $(\mathbf{A}, \mathbf{b})$ at any stage can be obtained in terms of those at any previous stage by means of a single matrix of transformation which is built up of matrix factors alternately of the type I and **R**.

In the case of reflection in a rotationally symmetrical system, we can write

$$\mathbf{A}' = \mathbf{A}$$

and

$$\mathbf{b}' = (R_{11} + R_{31}\mathbf{A}^2 + R_{41}\mathbf{A}\cdot\mathbf{b} + R_{51}\mathbf{b}^2)\,\mathbf{A} + (R_{21} + R_{61}\mathbf{A}^2 + R_{71}\mathbf{A}\cdot\mathbf{b} + R_{81}\mathbf{b}^2)\,\mathbf{b},$$

where the fourth and higher powers of **A** and **b** have been neglected in comparison with unity and the R_{ij}'s are constants to be determined from the law of reflection and the shape of the reflecting surface. In matrix notation

$$(\mathbf{A}', \mathbf{b}') = (\mathbf{A}, \mathbf{b}) \begin{pmatrix} 1 & R_{11} + R_{31}\mathbf{A}^2 + R_{41}\mathbf{A}\cdot\mathbf{b} + R_{51}\mathbf{b}^2 \\ 0 & R_{21} + R_{61}\mathbf{A}^2 + R_{71}\mathbf{A}\cdot\mathbf{b} + R_{81}\mathbf{b}^2 \end{pmatrix}.$$

The elements of this matrix of transformation are functions of the vectors on which the matrix operates and hence not suited for repeated operation when a number of transformations are involved. If, however, we apply the linear transformation to the vector row comprising all the first and third order terms in **A** and **b**, *i.e.*, $(\mathbf{A}, \mathbf{b};\ \mathbf{A}^2\mathbf{A}\ldots)$, we obtain an 8×8 matrix with constant elements. The first two terms of the vector row refer to paraxial optics and the subsequent six to the third order geometrical aberrations.

At any stage, $(\mathbf{A}', \mathbf{b}')$ can be determined as a function of the two paraxial and the six third order terms in **A** and **b**. Evidently, the coefficients of the terms corresponding to $\mathbf{A}'$ and $\mathbf{b}'$ will form the elements of the first two columns of the matrix of transformation, say **X**, of the complete vector

row. The other elements of **X** will then be functions of the paraxial elements only. It can be shown that **X**, the matrix of transformation at an arbitrarily chosen stage can be written in the form:

$$\mathbf{X} = \begin{array}{|c|c|} \hline \mathbf{X}_1 & \\ \hline \mathbf{X}_2 & \mathbf{X}_3 \\ \hline \end{array}$$

$$= \left|\begin{array}{cc|c} X_{11} & X_{12} & \\ X_{21} & X_{22} & \\ \hline X_{31} & X_{32} & \\ X_{41} & X_{42} & \\ X_{51} & X_{52} & \begin{pmatrix} X_{11} & X_{12} \\ X_{21} & X_{22} \end{pmatrix} \times \begin{pmatrix} X_{11}^2 & X_{11}X_{12} & X_{12}^2 \\ 2X_{11}X_{21} & (X_{11}X_{22} + X_{12}X_{21}) & 2X_{12}X_{22} \\ X_{21}^2 & X_{21}X_{22} & X_{22}^2 \end{pmatrix} \\ X_{61} & X_{62} & \\ X_{71} & X_{72} & \\ X_{81} & X_{82} & \end{array}\right| \quad (2)$$

where the zeros are not written. The above scheme of partitioning the matrices will be followed throughout the paper. The 2×2 submatrix at the left-hand top corner is the paraxial matrix. The submatrix at the right-hand bottom corner is a 6×6 matrix. The multiplication symbol implies the direct product of the two matrices. In other words, if the matrix

$$\begin{pmatrix} X_{11}^2 & \cdots & X_{12}^2 \\ \vdots & & \vdots \\ X_{21}^2 & \cdots & X_{22}^2 \end{pmatrix}$$

is denoted by **Q**, the matrix

$$\begin{pmatrix} X_{11} & X_{12} \\ X_{21} & X_{22} \end{pmatrix} \times \mathbf{Q}$$

is equal to

$$\begin{pmatrix} X_{11}\mathbf{Q} & X_{12}\mathbf{Q} \\ X_{21}\mathbf{Q} & X_{22}\mathbf{Q} \end{pmatrix}.$$

Thus, at any stage, only the first two columns of the matrix of transformation need be found out. The other elements which, however, are used in the multiplication process are completely determined in terms of the elements of the paraxial sub-matrix in the manner illustrated. Such considerations apply equally well to both reflection and refraction systems. Since we are interested in the former alone, our discussion is confined to that.

3. Notation

Quantities referring to ray intercepts and separation of reference planes should be taken as denoting actual lengths when printed in small letters but should be assumed to have been multiplied by the vertex curvature ρ, if they are printed in capitals or Greek letters, *e.g.*, **a** refers to the actual vector intercept of a ray on a reference plane, while **A** represents ρ**a**. Suffixes are attached to the vectors to indicate in which reference planes they are located, *e.g.*, *t*, *o*, *i* refer to the tangent plane at the vertex of the reflector, the object plane and the image plane respectively. When no suffixes are attached, the vectors are assumed to be situated in any arbitrarily chosen reference plane. Accented magnitudes refer to conditions after an interval or a reflection transformation.

Different surfaces are referred to by numbers 1, 2 and the numerical suffixes 1, 2.... are attached to magnitudes whenever it is necessary to specify to which surface they refer to. When more than one numerical suffix separated by a comma is attached to any quantity in an expression it is to be understood that the expression is valid for each one of the surfaces defined by the numerical suffix provided, however, that the corresponding quantities are chosen throughout the expression.

4. Analytical Deduction of the Possible Combinations of X-Ray Focussing Mirrors that can Form an X-Ray Image

In a previous communication (Thathachari and Ramachandran, 1952) it has been shown that the only possible combination of *spherical* crystal reflectors which can give X-ray images similar to those in optical microscopes is that in which both the mirrors are concave and form parts of the same spherical surface. Under these conditions, the Bragg relation is satisfied at both the mirrors for any number of multiple reflections. In what follows, we shall show that a combination of aspherical surfaces can form an X-ray image only for values of the aperture and field small enough to render their fourth and higher powers negligible when compared to the corresponding powers of the vertex radii of curvature of the reflectors.

We shall restrict ourselves to rotationally symmetrical systems. Let us consider a combination of two X-ray focussing mirrors 1 and 2. The condition for the formation of an X-ray image is that the Bragg relation should be satisfied simultaneously at both the reflectors. Taking first the axial ray, this condition will hold only if the lattice spacing for the reflecting planes is the same for both 1 and 2. In other words, both 1 and 2 should be of the same crystalline material and the lattice planes employed for the selective reflection of X-rays should have the same Miller indices in either case. When this is so, any other ray will satisfy the Bragg relation at both 1 and 2 only if it is equally inclined or inclined at supplementary angles to the normals to the reflecting surfaces at the respective points of incidence. In other words if **s** represents the unit vector along a ray and $\mathbf{n}_1$, $\mathbf{n}_2$ the unit normal at the points of incidence of this ray on 1 and 2 respectively, the required condition is

$$(\mathbf{s}\cdot\mathbf{n}_1)^2 = (\mathbf{s}\cdot\mathbf{n}_2)^2 \tag{3}$$

Fig. 1 represents the section of the system by a plane containing the optic axis OH and the point of incidence P of *a* ray on the reflecting surface.

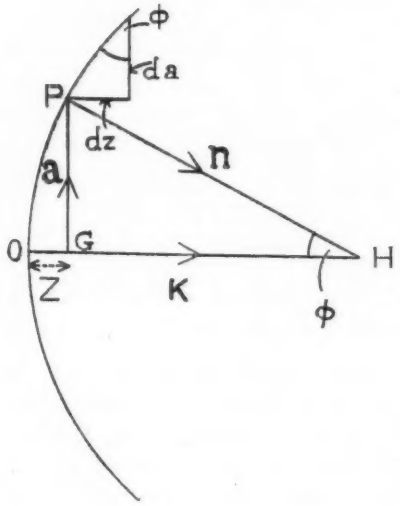

FIG. 1

G is the foot of the perpendicular from P on OH. PH is the normal to the surface at P.

Now, an axially symmetrical reflecting surface can be defined by

$$Z = z\rho = (\mathbf{A}^2/2) + (\lambda\mathbf{A}^4/8) + (\lambda'\mathbf{A}^6/16), \tag{4}$$

where ρ is the vertex curvature and z (= OG) is the separation between the vertex plane and the reference plane containing P and $\mathbf{A} = \rho\mathbf{a}$, where $\mathbf{a}$ is the vector GP. λ, λ' are constants which define the shape of the surface. If the reflecting surface is a conicoid of revolution $\lambda = (1 - e^2)$ and $\lambda' = \lambda^2 = (1 - e^2)^2$, where e stands for the eccentricity of the generating conic. The surface is thus a sphere if $\lambda = 1$, a paraboloid of revolution if $\lambda = 0$ and a spheroid or hyperboloid or revolution according as λ is positive (less than unity) or negative. The sixth and higher powers of $\mathbf{A}$ have been neglected as compared to unity.

The unit normal $\mathbf{n}$ to the surface at a point P defined by the vector a may be put in the form

$$\mathbf{n} = [1 - (\mathbf{A}^2/2) - \{(4\lambda - 3)\,\mathbf{A}^4/8\}]\,\mathbf{K} - [1 - \{(1 - \lambda)\,\mathbf{A}^2/2\} + \{3\,(\lambda' - 2\lambda + 1)\,\mathbf{A}^4/8\}]\,\mathbf{A} \tag{5}$$

Similarly, we have

$$(\mathbf{s}\cdot\mathbf{n}_{1,2})^2 = 1 - \mathbf{A}_{1,2}{}^2 - 2\mathbf{A}_{1,2}\cdot\mathbf{b} + (1 - \lambda_{1,2})\,\mathbf{A}_{1,2}{}^4 + (2 - \lambda_{1,2})\,\mathbf{A}_{1,2}{}^2\,(\mathbf{A}_{1,2}\cdot\mathbf{b}) + (\mathbf{A}_{1,2}\cdot\mathbf{b})^2 \tag{6}$$

(The derivations of the above expressions are given in Appendix I). Here $\mathbf{A}_{1,2}$ refers to a vector in the reference plane through the point of incidence. It will be convenient, however, to express it in terms of the intercept in a fixed reference plane, *viz.*, the vertex plane denoted by the subscript t. We know that

$$\begin{aligned}\mathbf{A}_{1,2} &= \mathbf{A}_{t1,2} + \mathbf{b}\,\{(\mathbf{A}_{1,2}{}^2/2) + (\lambda_{1,2}\,\mathbf{A}_{1,2}{}^4/8)\} \\ &= \mathbf{A}_{t1,2} + \mathbf{b}\,\{(\mathbf{A}_{t1,2}{}^2/2) + (\mathbf{A}_{t1,2}{}^2\,\mathbf{A}_{t1,2}\cdot\mathbf{b}/2) + (\lambda_{1,2}\mathbf{A}_{t1,2}{}^4/8)\}\end{aligned} \tag{7}$$

Making this substitution

$$(\mathbf{s}\cdot\mathbf{n}_{1,2})^2 = 1 - \mathbf{A}_{t1,2}{}^2 - 2\mathbf{A}_{t1,2}\cdot\mathbf{b} - \mathbf{A}_{t1,2}{}^2\mathbf{b}^2 + (1 - \lambda_{1,2})\,\mathbf{A}^2{}_{t1,2}\,(\mathbf{A}_{t1,2}\cdot\mathbf{b}) + (1 - \lambda_{1,2})\,\mathbf{A}_{t1,2}{}^4 + (\mathbf{A}_{t1,2}\cdot\mathbf{b})^2, \tag{8}$$

where

$$\mathbf{A}_{t1,2} = \rho_{1,2}\,\mathbf{a}_{t1,2}$$

the subscript t refers to quantities on the vertex plane and 1, 2 to the two surfaces. Let the ratio of the vertex curvature of the two mirrors be μ,

i.e., $\rho_2/\rho_1 = \mu$ and let d be the separation between the vertex planes of 1 and 2.

Let

$$D = \rho_1 d.$$

Then

$$\mathbf{A}_{t2} = \mu\,(\mathbf{A}_{t1} + \mathbf{b}D)$$

substituting this value of $\mathbf{A}_{t2}$ in (8) the following equation is obtained neglecting the sixth and higher powers of $\mathbf{A}_{t1,2}$ and $\mathbf{b}$ compared to unity

$$\begin{aligned}
&1 - \mathbf{A}_{t1}^2 - 2\mathbf{A}_{t1}\cdot\mathbf{b} + (1 - \lambda_1)\,\mathbf{A}_{t1}^4 - \mathbf{A}_{t1}^2\mathbf{b}^2 + (1 - \lambda_1)\mathbf{A}_{t1}^2\mathbf{A}_{t1}\cdot\mathbf{b}) \\
&\qquad + (\mathbf{A}_{t1}\cdot\mathbf{b})^2 \\
&= 1 - \mu^2\,(\mathbf{A}_{t1}^2 + 2D\mathbf{A}_{t1}\cdot\mathbf{b} + D^2\mathbf{b}^2) - 2\mu\,(\mathbf{A}_{t1}\cdot\mathbf{b} + D\mathbf{b}^2) \\
&+ (1 - \lambda_2)\,\mu^4\,\{\mathbf{A}_{t1}^4 + 4D^2\,(\mathbf{A}_{t1}\cdot\mathbf{b})^2 + D^4\mathbf{b}^4 + 4D\mathbf{A}_{t1}^2\mathbf{A}_{t1}\cdot\mathbf{b} \\
&\qquad + 4D^3\mathbf{b}^2\,(\mathbf{A}_{t1}\cdot\mathbf{b}) + 2D^2\mathbf{A}_{t1}^2\mathbf{b}^2\} \\
&- \mu^2\,\{\mathbf{A}_{t1}^2\mathbf{b}^2 + 2D\mathbf{b}^2\,(\mathbf{A}_{t1}\cdot\mathbf{b}) + D^2\mathbf{b}^4\} \\
&+ (1 - \lambda_2)\,\mu^3\,\{\mathbf{A}_{t1}^2\,(\mathbf{A}_{t1}\cdot\mathbf{b}) + 3D^2\mathbf{b}^2\,(\mathbf{A}_{t1}\cdot\mathbf{b}) + 2D\,(\mathbf{A}_{t1}\cdot\mathbf{b})^2 \\
&\qquad + D\mathbf{A}_{t1}^2\mathbf{b}^2 + D^3\mathbf{b}^4\} \\
&+ \mu^2\,\{(\mathbf{A}_{t1}\cdot\mathbf{b})^2 + 2D\mathbf{b}^2\,(\mathbf{A}_{t1}\cdot\mathbf{b}) + D^2\mathbf{b}^4\} \qquad (9)
\end{aligned}$$

Since the equation is to be true for all values of $\mathbf{A}_{t1}$ and $\mathbf{b}$, the coefficients of like terms on either side may be equated. First let us suppose that the square and higher powers of $\mathbf{A}_{t1}$ and $\mathbf{b}$ are negligible when compared to unity. This means that the aperture of the reflecting surface is so small that the surface can be identified with a sphere of curvature equal to its vertex curvature and the rays are all very close to the optic axis. Under these conditions it is found that the relation (3) holds good for any two surfaces, *i.e.*, for any curvature and for any separation. Let us, now, neglect only the fourth and higher powers of $\mathbf{A}_{t1}$ and $\mathbf{b}$ as compared to unity. Then the required condition is satisfied if $\mu = -1$ and $D = 2$, *i.e.*, if the two curvatures are equal in magnitude but opposite in sense and their vertices are separated by a distance equal to twice the vertex radius of curvature. There is, however, no restriction on the shape of the surfaces. When, however, the sixth and higher powers of $\mathbf{A}_{t1}$ and $\mathbf{b}$ become important the relation is obeyed only if $\lambda_1 = \lambda_2 = 1$; $\mu = -1$ and $D = 2$. The additional condition $\lambda_1 = \lambda_2 = 1$ means that both the surfaces should be spherical.

It has been shown in a previous article (Thathachari and Ramachandran, 1952) that the Bragg relation is rigorously obeyed by any ray simultaneously on both the mirrors *if they form parts of the same sphere* and there is no restriction whatever on the size of the aperture or the field. We now find that, as soon as the reflecting surfaces begin to deviate from spheres restrictions are brought about and the above relations can be satisfied only when the aperture and field, *i.e.*, $\mathbf{A}_t$ and $\mathbf{b}$ are sufficiently small, so that their fourth and higher power can be ignored in comparison with unity. In this case, the glancing angles θ, θ' of the same ray on the two mirrors are not equal. But if a Bragg reflection is to occur the difference of the two glancing angles, say $d\theta$, should be of the order of 10^{-6} radian. The consequent change in

$$(\mathbf{s}\cdot\mathbf{n}_1)^2 = \sin^2\theta$$

is given by

$$\sin 2\theta\, d\theta = \sin 2\theta/10^6$$

and is of the order of 10^{-6}. Since the fourth and higher powers of $\mathbf{A}_t$ and $\mathbf{b}$ are to be negligible in comparison with unity, we can roughly say that A_t^4 and b^4 should be of the order of 10^{-6}, *i.e.*, A_t and b should be of the order of 1/30. In other words, in the combinations of X-ray focussing mirrors which are not exactly spherical the radius of the aperture should be less than about 1/30 of the vertex radius of curvature.

5. Calculation of the Matrix Representing the Complete Passage of a Ray in a Multiple Reflection X-Ray Microscope

We have already shown that the interval matrix is given by

$$\begin{array}{|c|c|}\hline 1 & \\ \hline Z & 1 \\ \hline \end{array}$$

where Z is ρ times the separation of the two reference planes between which the transit of the ray takes place. Applying the linear transformation to the vector row $(\mathbf{A}, \mathbf{b};\ \mathbf{A}^2\mathbf{A}\ldots.)$ as illustrated in the general case, the interval matrix

$$\mathbf{I}(Z) = \begin{array}{|c|c|}\hline \begin{matrix}1 & \\ Z & 1\end{matrix} & \\ \hline & \begin{pmatrix}1 & \\ Z & 1\end{pmatrix} \times \begin{pmatrix}1 & & \\ 2Z & 1 & \\ Z^2 & Z & 1\end{pmatrix} \\ \hline \end{array} \qquad (10)$$

The reflection matrix can be shown to be (*vide* Appendix II)

$$\mathbf{R} = \left[\begin{array}{cc|c} 1 & -2 & \\ & -1 & \\ \hline 1 & -3 & \\ & -2 & \\ & 0 & \\ \hdashline & & \begin{pmatrix} 1 & -2 \\ & -1 \end{pmatrix} \times \begin{pmatrix} 1 & -2 & 4 \\ & -1 & 4 \\ & & 1 \end{pmatrix} \\ & \text{Do.} & \end{array}\right] \tag{11}$$

setting $\lambda = 1$ for a spherical reflector.

The submatrix $\mathbf{R}_2$ consists of two identical halves as indicated by the dotted line; this is true of all 8×8 matrices occurring hereafter. Having thus determined the fundamental factor matrices R and I (Z), we shall apply them to the study of the image formation due to N successive reflections from the mirrors 1 and 2 forming parts of the same spherical surface. As explained in Section 2 we shall adopt the sign convention that, for both 1 and 2, **K** is positive for the direction vertex to centre of the reflecting surface, for the reflection transformation at that surface and the subsequent interval transformation to the next surface. Thus, after the interval transformation of one mirror and before the reflection transformation at the other, the unit vector **K** reverses its sign. The matrix representing the reversal of **K** can be shown to reverse the sign of **b** and leave **A** unchanged. Let this matrix be denoted by **U**. Let **T** denote the matrix built up from the three factor matrices in the following order:—(1) the reflection matrix R, (2) the interval matrix between the vertex planes of the two mirrors I (2) since, in this case $Z = 2$ and (3) the matrix U representing the reversal of **K**.

T is then given by

$$\mathbf{T} = \left[\begin{array}{c|c} \begin{matrix} -3 & 2 \\ -2 & 1 \end{matrix} & \\ \hline \begin{matrix} -5 & 3 \\ -4 & 2 \\ 0 & 0 \end{matrix} & \\ \cdots\cdots & \begin{pmatrix} -3 & 2 \\ -2 & 1 \end{pmatrix} \times \begin{pmatrix} 9 & -6 & 4 \\ 12 & -7 & 4 \\ 4 & -2 & 1 \end{pmatrix} \\ \text{Do.} & \end{array}\right] \tag{12}$$

If **L** represents the complete matrix representing the passage of the ray from the vertex plane of the mirror causing the first reflection to the paraxial image plane after N reflections successively from the two mirrors, it is easily shown that

$$\mathbf{L} = (\mathbf{T})^{N-1}\mathbf{R}\mathbf{I}(\eta), \tag{13}$$

where $\mathbf{I}(\eta)$ represents the interval matrix representing the transit of the ray from the vertex plane of the mirror causing the Nth reflection to the paraxial image plane. $\eta = \rho\nu$, where ν is the corresponding separation. Following the scheme of partitioning shown in Eqn. (2) it is found that if r is an integer, the following relations hold:

$$(\mathbf{T})_1^r = (\mathbf{T}_1)^r$$

$$(\mathbf{T})_2^r = \sum_{s=0}^{r-1} (\mathbf{T}_3)^s (\mathbf{T}_2) (\mathbf{T})_1^{r-s-1}$$

and

$$(\mathbf{T})_3^r = (\mathbf{T}_3)^r$$

Now, by actual multiplication, we find that

$$(\mathbf{T}_1)^r = (-1)^r \begin{pmatrix} (2r+1) & -2r \\ 2r & -(2r-1) \end{pmatrix}$$

Hence $(\mathbf{T}_3)^r$ can be derived, as explained in Section 2, to be

$$(\mathbf{T}_3)^r = (-1)^r \begin{pmatrix} (2r+1) & -2r \\ 2r & -(2r-1) \end{pmatrix} \times \begin{pmatrix} (2r+1)^2 & -2r(2r+1) & 4r^2 \\ 4r(2r+1) & -(8r^2-1) & 4r(2r-1) \\ 4r^2 & -2r(2r-1) & (2r-1)^2 \end{pmatrix}$$

The matrices $(\mathbf{T}_3)^s$, $(\mathbf{T}_2)$ and $(\mathbf{T}_1)^{r-s-1}$ are all thus known and the elements of the submatrix $(\mathbf{T}_2)^r$ can be determined by working out the summation.

Thus the matrix $(T)^{N-1}$ is found to be

$$(T)^{N-1} \equiv (-1)^{N-1} \begin{array}{|c|c|} \hline (2N-1) & -(2N-2) \\ (2N-2) & -(2N-3) \\ \hline (N-1)(2N-1)(4N-3)/3 & -(N-1)(8N^2-16N+9)/3 \\ 4(N-1)(2N-1)(2N-3)/3 & -(N-1)(2N-3)(4N-5)/3 \\ 2(N-1)(N-2)(4N-3)/3 & -(N-1)(N-2)(2N-3)/3 \\ \hline \multicolumn{2}{|c|}{\text{Do.}} \\ \hline \end{array} \times \begin{pmatrix} (2N-1) & -(2N-2) \\ (2N-2) & -(2N-3) \end{pmatrix} \times \begin{pmatrix} (2N-1)^2 & -2(N-1)(2N-1) \\ 4(N-1)(2N-1) & -(8N^2-16N+7) \\ 4(N-1)^2 & -2(N-1)(2N-3) \\ & 4(N-1)^2 \\ & 4(N-1)(2N-3) \\ & (2N-3)^2 \end{pmatrix} \quad (14)$$

When N is equal to unity the above reduces to a unit matrix as it obviously should. The results can be checked by giving N different values and checking the results obtained by actual multiplication.

The factor $\mathbf{RI}(\eta)$ is found to be

$$\mathbf{RI}(\eta) = -\left|\begin{array}{cc|c} (2\eta-1) & 2 & \\ \eta & 1 & \\ \hline (3\eta-1) & 3 & \\ 2\eta & 2 & \\ 0 & 0 & \\ \hline & & \begin{pmatrix} (2\eta-1) & 2 \\ \eta & 1 \end{pmatrix} \times \begin{pmatrix} (2\eta-1)^2 & 2(2\eta-1) & 4 \\ 2\eta(2\eta-1) & (4\eta-1) & 4 \\ \eta^2 & \eta & 1 \end{pmatrix} \\ \text{Do.} & & \end{array}\right| \tag{15}$$

The complete matrix of transformation $\mathbf{L}$ is obtained by multiplying $(\mathbf{T})^{N-1}$ by $\mathbf{RI}(\eta)$ in the given order. Hence $\mathbf{A}_i$ (on the paraxial image plane) is obtained in terms of $\mathbf{A}_t$ and $\mathbf{b}$ as

$$\mathbf{A}_i = \mathbf{L}_{11}\mathbf{A}_t + \mathbf{L}_{21}\mathbf{b} + (\mathbf{A}_t + \mathbf{b})(\mathbf{L}_{31}\mathbf{A}_t^2 + \mathbf{L}_{41}\mathbf{A}_t \cdot \mathbf{b} + \mathbf{L}_{51}\mathbf{b}^2) \tag{16}$$

Since

$$\mathbf{L}_{31} = \mathbf{L}_{61};\ \mathbf{L}_{41} = \mathbf{L}_{71} \text{ and } \mathbf{L}_{51} = \mathbf{L}_{81}$$

By carrying out the above multiplication it is found that

$$\left.\begin{aligned} \mathbf{L}_{11} &= (-1)^N [2N\eta - (2N-1)] \\ \mathbf{L}_{21} &= (-1)^N [(2N-1)\eta - (2N-2)] \\ \mathbf{L}_{31} &= (-1)^N N[(8N^2+1)\eta - (8N^2 - 6N + 1)]/3 \\ \mathbf{L}_{41} &= (-1)^N 2N[(8N^2 - 6N + 1)\eta - (8N^2 - 12N + 4)]/3 \\ t_{51} &= (-1)^N N[(8N^2 - 12N + 4)\eta - (8N^2 - 18N + 10)]/3 \end{aligned}\right\} \tag{17}$$

We have thus obtained $\mathbf{A}_i$ as a power series in $\mathbf{A}_t$ and $\mathbf{b}$ containing terms upto the third order. $\mathbf{A}_i$ is the vector intercept of the ray on the image plane after N reflections successively from the two mirrors. $\mathbf{A}_t$ and $\mathbf{b}$ are vectors defining the incident ray: $\mathbf{A}_t$ is the vector intercept of the incident ray on the vertex plane of the mirror causing the first reflection (say 1) while $\mathbf{b}$ is a vector (also on the vertex plane of 1) of magnitude equal to the slope of the incident ray. In the subsequent sections we shall use the power

series deduced above to discuss the conditions for the paraxial image formation and to evaluate the third order aberrations.

6. Paraxial Theory Deduced as a Special Case

Let a point object be defined by the vector $\mathbf{a}_0$ in the object plane. Let u be the separation between the object plane and the vertex plane of the mirror causing the first reflection (say 1). Let

$$\xi = \rho u$$

consider a ray proceeding from the object point and defined by the vector $\mathbf{A}_t$ and $\mathbf{b}$ in the vertex plane of 1. Then by definition

$$\mathbf{b} = (\mathbf{A}_0 - \mathbf{A}_t)/\xi$$

substituting this value in the expression for $\mathbf{A}_i$, we find that

$$\begin{aligned}\mathbf{A}_i = {} & (\mathrm{L}_{11} - \mathrm{L}_{21}/\xi)\,\mathbf{A}_t + (\mathrm{L}_{21}/\xi)\,\mathbf{A}_0 \\ & + [(1 - 1/\xi)\,\mathbf{A}_t + (\mathbf{A}_0/\xi)]\,[\{\mathrm{L}_{31} - (\mathrm{L}_{41}/\xi) + (\mathrm{L}_{51}/\xi^2)\}\,\mathbf{A}_t^{\,2} \\ & + \{\mathrm{L}_{41} - 2\,(\mathrm{L}_{51}/\xi)\}\,(\mathbf{A}_t \cdot \mathbf{A}_0)/\xi + \{(\mathrm{L}_{51}\mathbf{A}_0^{\,2}/\xi^2)\}] \qquad (18)\end{aligned}$$

A point image will be obtained if the rays proceeding from the object point in different directions arrive at the same point in the image plane, after suffering a number of reflections. In other words, for a given $\mathbf{A}_0$, $\mathbf{A}_i$ should be independent of $\mathbf{A}_t$, *i.e.*, in the development of $\mathbf{A}_i$ as a power series in $\mathbf{A}_t$ and $\mathbf{A}_0$ all the terms containing $\mathbf{A}_i$ should vanish. The coefficients of powers of $\mathbf{A}_t$ and $\mathbf{A}_0$ are functions only of ξ, η and N and since ξ and N are fixed η will be the only variable and hence all the coefficients may not vanish simultaneously. If, however, we choose sufficiently small values of $\mathbf{A}_t$ and $\mathbf{A}_0$ so that their squares and higher powers can be neglected in comparison with unity (*i.e.*, for paraxial conditions) a point image will be obtained if the coefficient of $\mathbf{A}_t$ vanishes. The condition for this is

$$\mathrm{L}_{11} = \mathrm{L}_{21}/\xi$$

or

$$2N\eta - (2N - 1) = [(2N - 1)\,\eta - (2N - 2)]/\xi.$$

The magnification can be shown to be given by the coefficient of $\mathbf{A}_0$ which is

$$(\mathrm{L}_{21}/\xi) = (-1)^N\,[(2N - 1)\,\eta - (2N - 2)]/\xi.$$

The image is erect or inverted according as this coefficient is positive or negative. Let

$$[(2N - 1)\,\eta - (2N - 2)]/\xi = M = [2N\eta - (2N - 1)]$$

Then we have the following expressions for ξ and η in terms of M and N

$$\left.\begin{aligned} &\xi = [(2N-1)\,M+1]/2NM \\ \text{and}\quad &\eta = (M+2N-1)/2N \end{aligned}\right\} \tag{19}$$

The image will be real if $\eta > 0$.

This is possible for all positive values of M. When M is negative the magnification ranges between $1/(2N-1)$ and $(2N-1)$ since the condition for real images, namely, $\eta > 0$ requires that $|M| < (2N-1)$, while the condition for a real object, namely, $\xi > 0$ requires that $|M| < 1/(2N-1)$.

We shall henceforth consider only the case $M > 0$, since here there is no restriction on the values that the magnification can assume. When M is positive the real image is erect for an even number of reflections and inverted for an odd number of reflections. It is the other way about for negative values of M.

The effective length of the optical path in the microscope is given by

$$(\eta/\rho) = (M+2N-1)/2N\rho.$$

If the same magnification is obtained in a single stage, the length will be

$$(M+1)/2\rho$$

Thus, magnification remaining the same, the length of the optical path is reduced in the ratio

$$[1+2\,(N+1)/(M+1)]/N \simeq 1/N \text{ (for } N \ll M).$$

These results are in accordance with those reported in the earlier paper.

7. Theory of the Third Order Aberrations for Multiple Reflections

When the third and higher powers of $\mathbf{A}_t$, $\mathbf{A}_0$ become important, $\mathbf{A}_i$ is different values of $\mathbf{A}_t$. Hence rays proceeding from the object point in different directions do not focus at the paraxial image point and thus a patch is obtained instead of a point image, the size of the patch being a measure of the aberration. If $\mathbf{A}_t$, $\mathbf{A}_0$ are taken as a measure of the maximum aperture and field employed, the third order aberrations can be classified under four heads according to the powers in aperture and field to which their magnitudes are proportional.

Aberration	Power in aperture	Power in field
Spherical aberration	3	0
Coma	2	1
Field errors	1	2
Distortion	0	3

From the above table it is easily seen that spherical aberration is the only aberration which is independent of the distance of the object point from the optic axis and hence is the only error for an axial point. In microscopy we usually have to deal with a small field and a large magnification. Under these conditions spherical aberration is the only prominent image defect. We shall therefore confine our attention to the study of this aberration alone. It can be shown that the aberration figure in this case is a circle of confusion around the paraxial image point, of radius proportional to the cube of the aperture radius and the square of the vertex curvature, the constant of proportionality being given by the coefficient of $A_I{}^2A_{II}$ in the expression for A_s and designated as the coefficient of spherical aberration S_N

$$S_N = (1 - 1/\xi)\,[L_{31} - (L_{41}/\xi) + (L_{51}/\xi^2)] \tag{20}$$

Substituting for η in terms of M and N, we have

$$\left.\begin{aligned} L_{31} &= (-1)^N\,[(8N^2 + 1)\,M + (4N^2 - 1)]/6 \\ L_{41} &= (-1)^N\,[(8N^2 - 6N + 1)\,M + (4N^2 - 1)]/3 \\ L_{51} &= (-1)^N\,[(8N^2 - 12N + 4)\,M + (4N^2 - 4)]/6 \end{aligned}\right\} \tag{21}$$

Substituting these values and expressing ξ in terms of M and N it is found that

$$|S_N| = (M-1)^2\,[(4N^2 - 1)\,(M^2 + M + 1) + 3M]/6\,[(2N - 1)\,M + 1]^3 \tag{22}$$

For the same magnification and the same aperture, the spherical aberration when a single reflection is employed is proportional to S_1 obtained by setting $N = 1$ in S_N

$$|S_1| = (M-1)^2/2\,(M+1) \tag{23}$$

$$|S_N|/|S_1| = (M+1)\,[(4N^2 - 1)\,(M^2 + M + 1) + 3M]/3\,[(2N-1)\,M + 1]^3$$

when $M \gg 1$

$$| S_N | / | S_1 | = (2N + 1)/3\,(2N - 1)^2 \qquad (24)$$

Thus for the same magnification and the same aperture, the spherical aberration is very much reduced when more than one reflection is employed. For large N $| S_N | / | S_1 |$ tends to zero. Even for N=2, $| S_2 | / | S_1 | = 1/5 \cdot 4$. This is an interesting result and a simple qualitative explanation is given below. We know that spherical aberration is independent of the distance of the object point from the axis. Hence we shall consider, without loss of generality, an axial point and estimate the spherical aberration contributed by each reflection by assuming that the image formed by the previous reflection is a point image serving as a point source for this reflection. Then we know that the radius of the circle of confusion due to the spherical aberration produced by the rth reflection is proportional to (*a*) M_r, where M_r stands for the magnification produced by the rth reflection and (*b*) the cube of the radius of the aperture used in this reflection. Now M_r can be put in the form

$$M_r = M'/M'',$$

where M' is the magnification up to and including the rth stage and M'' is the total magnification up to the $(r - 1)$th stage. Obviously,

$$M' = M_1 M_2 \ldots . M_r$$

and

$$M'' = M_1 M_2 \ldots . M_{r-1}$$

we have

$$\xi = [(2r - 1)\,M' + 1]/2rM' = [(2r - 3)\,M'' + 1]/2\,(r - 1)\,M''$$

Hence

$$M' = 1/[1 - \{r\,(1 - 1/M)/N\}]; \quad M'' = 1/[1 - \{(r - 1\,(1 - 1/M)/N\}]$$

Hence

$$M_r = 1 + (1 - 1/M)/[N - r\,(1 - 1/M)]$$

which reduces to

$$M_r = 1 + 1/(N - r) \qquad (25)$$

we see that the magnification is mainly at the last (Nth) stage since M_r is very small except when $r = N$. Even for $r = (N - 1)$ $M_r = 2$. Hence we can roughly say that the contribution to the spherical aberration is also mainly at the last (Nth) reflection.

Let ${}_r\mathbf{a}_t$ denote the radius of the aperture at the rth reflection ρ_r ${}_r\mathbf{a}_t = {}_r\mathbf{A}_t$ can be determined from the matrix $(\mathbf{T})^{N-1}$. Neglecting third order terms

$${}_r\mathbf{A}_t = (-1)^{r-1}\,[(2r - 1)\,{}_1\mathbf{A}_t + (2r - 2)\,\mathbf{b}]$$

Substituting $\mathbf{b} = -({}_1\mathbf{A}_t/\xi)$. For an axial point, and putting $\xi = 1 - \frac{1}{2}N$ for a large M, this becomes

$$ {}_r\mathbf{A}_t = (-1)^{r-1}\,[2(N-r)+1]\,{}_1\mathbf{A}_t\,/(2N-1) \qquad (26) $$

Thus the effective aperture is decreasing at each reflection and at the Nth reflection it is equal to $1/(2N-1)$ of that at the first reflection. Since the radius of the circle of confusion due to spherical aberration varies as the cube of the aperture radius, the contribution to the spherical aberration which is mainly at the last stage is $1/(2N-1)^3$ times that at a single stage with the same magnification and an aperture equal to that at the first stage. But at each stage there is some spherical aberration, however small and the sources for the successive reflections are not point sources. This explains why the ratio $(|\,S_N\,|/|\,S_1\,|)$ is not so small as $(2N-1)^{-3}$ but is actually equal to $(2N+1)/3\,(2N-1)^2$.

We have shown that when N reflections are employed the effective optical path in the microscope is reduced to $1/N$ of that when the same large magnification is obtained in a single stage. The further advantage is that the prominent image defect, *viz.*, spherical aberration, is appreciably reduced by increasing the number of reflections. By restricting the field to small values, the other image errors (*viz.*, the field errors) which show an increase as N is increased can be made negligibly small.

8. The Resolving Power of X-Ray Microscopes Employing Laue Reflections

The resolving power of a microscope is limited mainly by the blurring of the image due to (1) diffraction effects produced by the restriction of the light waves by a stop and (2) the image defects (the geometrical aberrations).

Due to the former case, it is known that two object points separated by a distance x can be resolved only if

$$ x \geqslant \lambda/2 \sin\phi, $$

where λ is the wavelength of the illuminating rediation and ϕ the angle between the incident ray and the optical axis.

($\sin\phi$ is called the " numerical aperture ")

Then

$$ \sin\phi \simeq A_t/\xi, $$

where $\mathbf{A}_t$ and ξ retain their significance as before.

For large magnification

$$\xi = (1 - \quad /2N)$$

Hence

$$\sin \phi = 2NA_t/(2N - 1)$$

Thus

$$x \geqslant (2N - 1)\, \lambda/4NA_t$$

Taking λ to be on an average 1Å and $A_t = 1/100$, for large values of N x has a maximum

$$x \geqslant 50 \text{ Å}$$

Thus considering diffraction effects alone, object points separated by a distance greater than 50 Å can be resolved by X-ray microscopes using Laue reflections.

For objects close to the axis, the only prominent image defect is spherical aberration and an approximate idea of the limitation of the resolving power due to this cause is furnished by geometrical optics. We have shown that a point object gives rise to a circle of confusion around the Gaussion image of radius equal to $MA_t^3R/2$. We shall (arbitrarily) suppose that two object points can be resolved if their Gaussion image points are separated by a distance greater than the diameter of the circle of confusion, *i.e.*, MA_t^3R. The corresponding distance for resolution in the object is given by $x \geqslant A_t^3R$. Due to practical difficulties R cannot be made as small as we please. We shall set $R = 10$ cm. as a practical lower limit. Then due to spherical aberration the minimum value of x will be 1,000 Å for $A_t = 1/100$. This can be reduced by a factor $(2N + 1)/3\ (2N - 1)^2$ if N reflections are employed.

For a single reflection therefore the limit of resolution is mainly set by spherical aberration. However if say 5 successive reflections are used, then the lower limit of x arising from this cause becomes about 45 Å which is of the same order as that due to diffraction. Such a microscope should theoretically resolve objects having a separation larger than about 50 Å.

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Summary

It is shown that ideally Bragg reflections can occur successively from two surfaces only if they form parts of the same sphere, a result shown to be

sufficient (but not necessary) in an earlier publication. However, if the aperture radius and the size of the object are small compared to the radius of curvature of the reflecting surfaces (such that fourth and higher power of their ratios are less than (10^{-6}), then the combination will work even with aspherical surfaces, provided the two reflectors are surfaces of revolution about a common axis and they are both concave reflectors having the same vertex radius of curvature and are separated by a distance equal to twice this radius. If a combination of two such mirrors are used, and N multiple reflections obtained with them, then the optical path is reduced appreciably (approximately as $1/N$) and the spherical aberration is also decreased (being proportional to $1/N$) for large magnifications. The resolving power of such a combination should be of the order of 50 Å. A combination of X-ray mirrors in the form of an X-ray microscope has, therefore, distinct advantages and it appears that the problem of realising such a unit in practice is worth investigating.

APPENDIX I

EXPRESSION FOR THE UNIT NORMAL

Consider a section of the surface by a plane containing the optic axis and the point P (of Fig. 1). The unit normal $\mathbf{n}$ at P is given by

$$\begin{aligned}\mathbf{n} &= (l\rho\mathbf{K} - \mathbf{A})/\rho\mathrm{PH} \\ &= (l\rho\mathbf{K} - \mathbf{A})/(\mathbf{A}^2 + l^2\rho^2)^{\frac{1}{2}} \\ &= (\mathbf{K} - \mathbf{A}/l\rho)/[1 + (\mathbf{A}/l\rho)^2]^{\frac{1}{2}},\end{aligned}$$

where l denotes the length GH

Now

$$(A/l\rho) = \tan\phi = dZ/dA$$

But

$$Z = (\mathbf{A}^2/2) + (\lambda\mathbf{A}^4/8) + (\lambda'\mathbf{A}^6/16)$$

Hence

$$(A/l\rho) = dZ/dA = [1 + (\lambda A^2/2) + (3\lambda' A^4/8)]\, A$$

In three dimensions

$$(\mathbf{A}/l\rho) = [1 + (\lambda\mathbf{A}^2/2) + (3\lambda'\mathbf{A}_t/8)]\,\mathbf{A}$$

Substituting this value of $(\mathbf{A}/l\rho)$ in (27) and ignoring the sixth and higher powers of $\mathbf{A}$ in comparison with unity, we have

$$\begin{aligned}\mathbf{n} = [1 - (\mathbf{A}^2/2) - \{(4\lambda - 3)\,\mathbf{A}^4/8\}]\,\mathbf{K} - [1 - \{(1 - \lambda)\,\mathbf{A}^2/2\} \\ + \{3\,(\lambda' - 2\lambda + 1)\,\mathbf{A}^4/8\}]\,\mathbf{A}\end{aligned}$$

If now, the fourth and higher powers of **A** are neglected in comparison with unity, we have

$$\mathbf{n} = [1 - (\mathbf{A}^2/2)]\,\mathbf{K} - [1 - \{(1 - \lambda)\,\mathbf{A}^2/2\}]\,\mathbf{A}$$

By definition

$$\mathbf{b} = [\mathbf{s} - \mathbf{K}\,(\mathbf{K}\cdot\mathbf{s})]/(\mathbf{K}\cdot\mathbf{s})$$

Since

$$\mathbf{s}^2 = 1 \text{ and } (\mathbf{K}\cdot\mathbf{b}) = 0$$

$$\mathbf{s} = (\mathbf{b} + \mathbf{K})/(1 + \mathbf{b}^2)^{\frac{1}{2}}$$

Hence

$$(\mathbf{s}\cdot\mathbf{n}_{1,2})^2 = [1 - \mathbf{A}_{1,2}{}^2 - 2\mathbf{A}_{1,2}\cdot\mathbf{b} + (1 - \lambda_{1,2})\,\mathbf{A}_{1,2}{}^4 + (2 - \lambda_{1,2})\,\mathbf{A}_{1,2}{}^2\,(\mathbf{A}_{1,2}\cdot\mathbf{b}) + (\mathbf{A}_{1,2}\cdot\mathbf{b})^2]/(1 + \mathbf{b}^2).$$

APPENDIX II

Derivation of the Reflection Matrix

Since we are taking the vertex planes as the reference planes and not the reflecting surfaces themselves, we shall separate the reflection matrix **R** into three factors, *viz.*, (1) the interval matrix representing the transit of the ray from the vertex plane to the reference plane containing the point of incidence. This is obtained by setting $Z = \mathbf{A}^2/2$ in $\mathrm{I}(Z)$; (2) the reflection matrix at the point of incidence and (3) the interval matrix representing the transit of the ray from the reference plane containing the point of reflection back again to the vertex plane. This is obtained by setting

$$Z = -\,\mathbf{A}^2/2 \text{ in } \mathrm{I}(Z),$$

The second factor is obtained from the law of reflection, *viz.*,

$$\mathbf{n}\times\mathbf{s} = \mathbf{n}\times\mathbf{s}',$$

where **s**, **s**′ are the unit vectors along the incident and reflected rays respectively and **n** is the unit normal to the surface at the point of incidence. The solution is **s**′

$$\mathbf{s}' = \mathbf{s} + \alpha\mathbf{n},$$

where

$$\alpha = -\,2\mathbf{s}\cdot\mathbf{n}.$$

Hence

$$\mathbf{b}' = \{\mathbf{s} - \mathbf{K}\,(\mathbf{K}\cdot\mathbf{s}')\}/\mathbf{K}\cdot\mathbf{s}'$$

$$= [\mathbf{b} + (\alpha/\mathbf{K}\cdot\mathbf{s})\,\{\mathbf{n} - \mathbf{K}\,(\mathbf{K}\cdot\mathbf{n})\}]/[1 + (\alpha/\mathbf{K}\cdot\mathbf{s}\,(\mathbf{K}\cdot\mathbf{n}]$$

$$\mathbf{s}/\mathbf{K}\cdot\mathbf{s} = \mathbf{b} + \mathbf{K}$$

and

$$\mathbf{n} = \{1 - (\mathbf{A}^2/2)\}\,\mathbf{K} - [1 - \{(1 - \lambda)\,\mathbf{A}^2/2\}]\,\mathbf{A}$$

for values of **A** sufficiently small so that its fourth and higher powers may be neglected in comparison with unity. Hence,

$$\mathbf{A}' = \mathbf{A}$$

$$\mathbf{b}' = -[\{2 + (2 + \lambda)\mathbf{A}^2 + 2\mathbf{A}\cdot\mathbf{b}\}\mathbf{A} + \{1 + 2\mathbf{A}^2 + 2\mathbf{A}\cdot\mathbf{b}\}\mathbf{b}].$$

The corresponding matrix factors is

$$\begin{pmatrix} 1 - \{2 + (2 + \lambda)\mathbf{A}^2 + 2\mathbf{A}\cdot\mathbf{b}\} & \\ 0 - \{1 + 2\mathbf{A}^2 + 2\mathbf{A}\cdot\mathbf{b}\} & \end{pmatrix}$$

The complete reflection matrix is hence obtained as

$$\begin{pmatrix} 1 + \mathbf{A}^2 - \{2 + (2 + \lambda)\mathbf{A}^2 + 2\mathbf{A}\cdot\mathbf{b}\} & \\ \mathbf{A}^2 \quad - \{1 + 3\mathbf{A}^2 + 2\mathbf{A}\cdot\mathbf{b}\} & \end{pmatrix}$$

Applying the linear transformation to the vector row $(\mathbf{A}, \mathbf{b}; \mathbf{A}^2\mathbf{A}\ldots.)$ the reflection matrix R is obtanied as

$$\mathbf{R} = \left[\begin{array}{cc|c} 1 & -2 & \\ & -1 & \\ \hline 1 & -(2+\lambda) & \\ & -2 & \\ & 0 & \begin{pmatrix} 1 & -2 \\ & -1 \end{pmatrix} \times \begin{pmatrix} 1 & -2 & 4 \\ & -1 & 4 \\ & & 1 \end{pmatrix} \\ \hdashline 1 & -3 & \\ & -2 & \\ & 0 & \end{array}\right]$$

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KINETICS OF INACTIVATION OF INVERTASE

By K. S. G. Doss,* F.A.Sc. and H. C. Saraswat §

(Indian Institute of Sugar Technology, Kanpur)

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Introduction

Many of the physico-chemical properties of invertase are found to be dependent on hydrogen-ion concentration. For instance the spreading power[1] of invertase on aqueous substratum is reduced by over 90% as the pH of the substratum is changed from 1·0 to 2·0. Similarly the rate of accumulation[2] of invertase at the surface of aqueous solutions comes down tremendously as the pH is raised from 1·0 to 3·0. Further the inversion activity of invertase is found to be a function of pH. The work of Euler and Laurin[3] has shown that inactivation of invertase is also a function of pH. The present paper gives an account of some detailed observations on inactivation.

Experimental

1. *Materials used.*—(*a*) The sample of invertase used was supplied by Messrs. Sugar Manufacturers' Supply Co. Ltd., 7–8, Idol Lane, London. The invertase concentrate is prepared from baker's yeast. The solution contains nearly 55% of purest glycerine for stabilization of the enzyme. The solution is clear and transparent and colourless. The activity is found to be constant for a long period. The solution does not contain any surface-active substance or nitrogenous compound. These details were kindly supplied by Messrs. Sugar Manufacturers' Supply Co., Ltd., London. The nitrogen content of the invertase concentrate is found to be $0{\cdot}65 \pm 0{\cdot}06$ mg./c.c.

Further, the spreading properties of this invertase concentrate are found to be practically the same as those of pure preparation used by Gorter and Dieu in their studies.[4] We have also prepared a purified product by adsorption of the commercial sample on alumina and elution by Na_2HPO_4.[5] The purified product also gave results not appreciably differing from that of the original product, whenever a check was made. There appears to be no

* Professor of Chemistry, Indian Institute of Sugar Technology, Kanpur.

§ Professor of Chemistry, Christ Church College, Kanpur.

doubt that all the main features of the results reported here will be reproduced by any similar purified product.

(*b*) The copper reagent was prepared and standardised according to the usual method.[6]

(*c*) The chemicals used were of Reagent quality of Merck.

2. *Method of finding out the activity of invertase.*—Our invertase preparation had a time value of 58 minutes per c.c. In the present work we have taken arbitrarily the activity of the invertase present in 1 c.c. of this preparation as 100 units. We have measured the activity of the other products dealt with in this paper in terms of this arbitrary standard. In comparing the activities of the various products with that of the original stock solution we have discarded the time value method since (*a*) the method takes a long time and is rather laborious; (*b*) it requires a large quantity of invertase preparation; and (*c*) the end point corresponds to an advanced stage of inversion of sugar in that it represents the stage at which 75·9% of sugar has been inverted. In view of this we have preferred the method of Gorter and Dieu[7] with some modifications.

The principle of the method consists in finding out the number of milligrams of invert sugar produced by different quanttiies of the stock invertase preparation (time value 58 minutes per c.c.; invertase content assumed arbitrarily as 100 units per c.c.) by following a special experimental procedure. A graph is then constructed by plotting the number of milligrams of invert sugar produced against the number of arbitrary units of invertase used. The activity of any other preparation can then be found out by determining the number of milligrams of invert sugar produced under the special experimental conditions and referring to graph (Fig. 1).

The following procedure is adopted for carrying out the inversions for determining the activity of invertase preparations. 10 c.c. of 20% sugar solution is taken in a large diameter tube which is kept in a thermostat at 25° C. To this are added 7 c.c. of acetate buffer solution pH 4·5 and $(8 - x)$ c.c. of distilled water and x c.c. of invertase preparation under test. The mixture is kept at 25° C. for 5 minutes and then the reaction is stopped by adding excess of M/4 caustic soda solution (final pH 11). The solution thus obtained is made up to 250 c.c. in a measuring flask. 5 c.c. of this dilute solution are withdrawn and added to 5 c.c. of copper reagent or a multiple of this volume, contained in a large test-tube. After mixing the solutions the tube is placed in boiling water and heated for 15 minutes. The tube is cooled quickly by immersing in ice-cold water. The unreduced copper is determined without filtration by dissolving about 2 to 3 grams

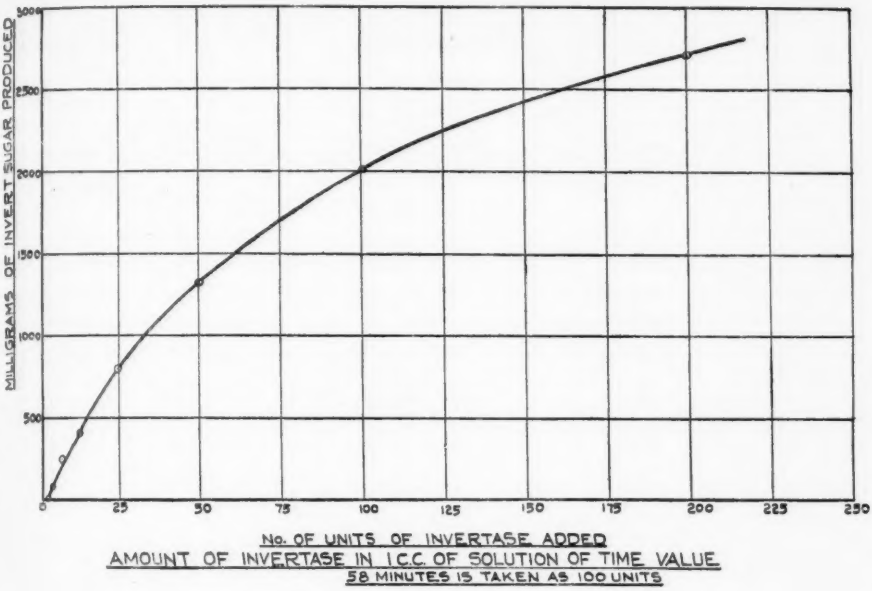

FIG. 1

of potassium iodide in it and acidifying it by 2M sulphuric acid. 5 c.c. of saturated potassium oxalate solution are added to stabilize the reaction.[8] After waiting for 5 minutes the liberated iodine is titrated against 0·1 N sodium thiosulphate using starch as indicator near the end point. The total copper in 5 c.c. of copper reagent is determined by a second titration with the copper reagent only. The difference between the two titration results is equivalent to the cuprous oxide precipitated by reducing sugar. Each c.c. of the difference indicates 6·36 milligrams of copper. The corresponding amount of reducing sugar is found from Munson and Walker Tables.[9]

To take into account any invert sugar that may be produced due to agencies other than invertase during the experimental determination of activity a blank is performed. This is done by taking 10 c.c. of 20% sugar solution without invertase and carrying out the whole experiment as before.

3. *Inactivation of invertase by changes in pH.*—For studying inactivation of invertase, the enzyme was introduced at a concentration of 2·5 units per c.c. in a medium of any required pH. 10 c.c. samples were drawn out at different intervals of time, the pH was quickly restored to 4·5 and their activity determined as described before. The results are given in Table I.

TABLE I

Inactivation of Invertase

Initial activity of invertase = 1/58 invertase units per c.c.

[Time value = 58 minutes per c.c.]

Activity of invertase at pH 4·5 after treatment, as a fraction of initial activity.

Time of treatment minutes	pH of the solution							
	1·29	1·34	1·38	1·58	1·78	2·3	3·02	4·5
5	0·05	0·2	0·55	0·625	0·875	0·95	0·925	1·05
10	0·025	0·03	0·425	0·55	0·775	0·85	0·95	1·05
20	0·025	0	0·225	0·525	0·775	0·85	0·95	..
30	0·02	0	0·15	0·475	0·775	0·85	0·95	1·05
40	0·016	0	0·05	0·4	0·775	0·85	0·95	..
50	0	0	0·03	..	..	..	..	..
60	0·01	0	0	..	..	0·85	0·95	1·03

Discussion

Effect of pH on inactivation of invertase.—An examination of Table I shows that invertase is very stable at pH 4·5. As the pH is lowered to a critical value inactivation becomes exceedingly fast. This critical pH is found to be in the neighbourhood of about 1·8. At a pH of 1·3 and below there is a loss of activity of over 95% in 5 minutes time whereas at pH 1·8 the loss is only about 12% within the same time. The inactivation process has been shown to be not due to adsorption as vessels of different size did not effect the extent of inactivation. Similarly the transfer of solution from vessel to vessel, at low pH so as to come into contact with a large surface of glass did not affect the activity. The inactivation is not following the simple first order formula. There is a high initial rate of inactivation which is followed by a slow rate of inactivation.

There appear to be two processes occurring simultaneously though independently bringing about the inactivation of invertase. Only one of these processes comes into operation at comparatively high pH ($\geqslant 1{\cdot}78$) and is very fast. In the first 5 minutes the inactivation due to this cause would be practically over. The other process begins to be effective only at lower pH and has a measurable rate at a pH of 1·58. At still lower pH,

both the processes are occurring fast and the inactivation is extremely quick. Further work is needed to elucidate the nature of the two processes.

Acknowledgement

The authors take this opportunity to thank Professor J. M. Saha, Director, Indian Institute of Sugar Technology, Kanpur, for his kind interest in the work.

Summary

A detailed study has been made of the kinetics of inactivation of invertase at 25° C. in acid media. The results indicate the existence of two processes, one of them being very fast and coming up at comparatively high pH values and the other coming up at lower pH.

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STUDIES IN SOIL PERMEABILITY

Part I. The Effect of Heating the Soil on Permeability Under Prolonged Submergence of Soil in Water

By K. Subba Rao and S. K. Wadhawan

[*Defence Science Organisation, Ministry of Defence, New Delhi (India)*]

Introduction

Soil permeability is a fundamental physical property which finds application in several engineering and agricultural operations. The problems like drainage, reclamation of saline soils, water spreading and storage underground, settlement of structures on saturated soils, excavations and construction of roads and air ports have a bearing on soil permeability.

A review of the literature on the subject indicates that an extensive study has been made by different workers[1, 3, 4, 5, 6, 8] on the various aspects of soil permeability. Christiansen[5] has studied the permeability characteristics of saline and alkali soils. Neal[8] has studied soil structure in relation to permeability. The effect of the micro-organisms which are normally present in the soil, on the permeability of soils under prolonged submergence in water has been studied by Allison[1] by employing both the sterilised and unsterilized soils and a number of sterilizing agents. That the changes in permeability depend not only on the nature of the soil but also on the composition of water has been shown by Christiansen.[5] The effect of entrapped air in the soil and also its removal by vacuum or displacement by carbon dioxide on the changes in permeability with time have been investigated by Christiansen, J. E.[7] and Christiansen, J. E., Fireman, M. and Allison.[6]

The effect of heating the soil on its permeability under prolonged submergence of the soil in water has not been investigated and a study of this aspect of the problem has revealed several interesting characteristics.[10]

Experimental

The Soil.—The Gangetic alluvial soil of Delhi (India) was chosen for the study. The soil was dug out at a depth of one foot from the surface. The season during which the soil sample was taken out was summer (June end) just before the commencement of monsoon.

The soil lumps were removed from the pit, pressed and rubbed between cardboard sheets and next sieved. The soil sample passing through 1 mm. sieve was chosen for permeability measurements.

Air Drying of the Soil.—The sieved sample was spread and kept exposed for 3 days for air drying. The air dry soil constituted the stock from which samples were taken out periodically for permeability studies.

Water Content of the Soil.—The water content of the air-dry soil was determined by heating a known weight of the soil in an oven at 105° C. for 2 hours. The water content was found to be 1·54% calculated on the weight of the dry soil.

Permeability Technique.—The permeability technique has been discussed by Fireman.[7] The constant water level method has also been adopted by Christiansen[4] and Allison.[1]

A brief description of the experimental technique employed in the present study is given below and is indicated in Fig. 1. The constant water level method was adopted in the measurement of permeability.

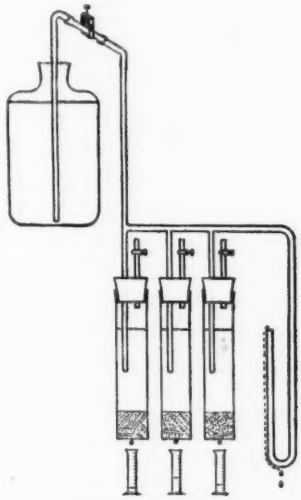


FIG. 1. Soil Permeability Apparatus.

The water reservoir consisted of three or more carboys filled with distilled water and interconnected. Such a big capacity was found to be useful in reducing to the minimum the fall in level of water in the reservoir when kept overnight.

The permeameter consisted of a pyrex glass tube about one inch in diameter and one foot in length. The exact diameter was determined by means of a travelling microscope. The bottom of each tube was ground on an emery paper to get a levelled surface. The tube was fitted with a

rubber cork carrying a stopcock and a T tube. The T tube was helpful in connecting a number of permeameter tubes in series along with the reservoir. The constant level overflow tube enabled the maintenance of constant water level in all the permeameter tubes. The function of the stopcock was to adjust easily the level of water inside the permeameter tubes if there was any variation in the level at any stage.

The ground end of the permeameter tube was covered with a muslin cloth which was fastened by a thread. The soil was introduced into the permeameter tube upto a height of 5 cm. through an inner tube. This inner tube was slowly rotated as the soil was being introduced in order to obtain uniform distribution. A water column of 10 cm. was maintained above the surface of the soil. The lengths of the soil column and heights of water head were kept the same in all the tubes.

Ordinarily within 15 minutes after the water was introduced from the reservoir into the permeameter tubes, complete soaking of the soil would take place. Therefore in all these experiments the first reading of permeability was taken after this interval of 15 minutes. The rate of flow of water through the constant level overflow tube was controlled by means of a pinchcock.

For measuring permeability, the water passing through the soil was collected in a measuring cylinder kept below the permeameter tube. The volume of water collected over an interval of 15 minutes was measured. These measurements were taken at intervals of about 8 to 10 hours. Permeability measurements were continued over several days and weeks.

Permeability Coefficient.—The permeability coefficient was calculated from Darcy's equation (6),

$$Q = \frac{PAH}{L},$$

where Q = Volume of water passing through the soil per second.

P = Permeability coefficient in cm. per second.

A = Cross section of the permeameter tube in sq. cm.

H = Height of water column in cm.

L = Length of the soil column in cm.

As the permeability coefficient calculated per second was found to be too small, the permeability in cm. per hour was chosen as the unit. Therefore Q is the volume of water collected per hour. H and L were equal to 15 cm. and 5 cm. respectively. For each tube, the diameter was measured by means of a travelling microscope and from this A was calculated.

The permeability coefficient obtained from the above equation is plotted against time and the progressive variations in permeability coefficient with time have been indicated in Figs. 2, 3, 4, 5.

Air Thermostat.—It is reported that permeability increases by 2·5% per degree rise of temperature.[5] This is obvious in view of the fact that permeability is essentially a capillary flow phenomenon and that the capillary flow as governed by Poiseuille's law is dependent upon the viscosity of the

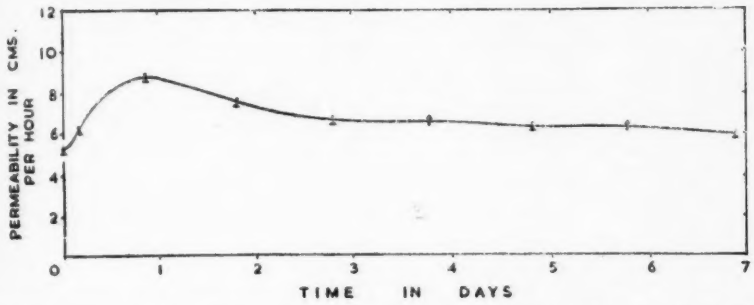


FIG. 2. Reproducibility of permeability Measurements on two samples of soil at 35° C.

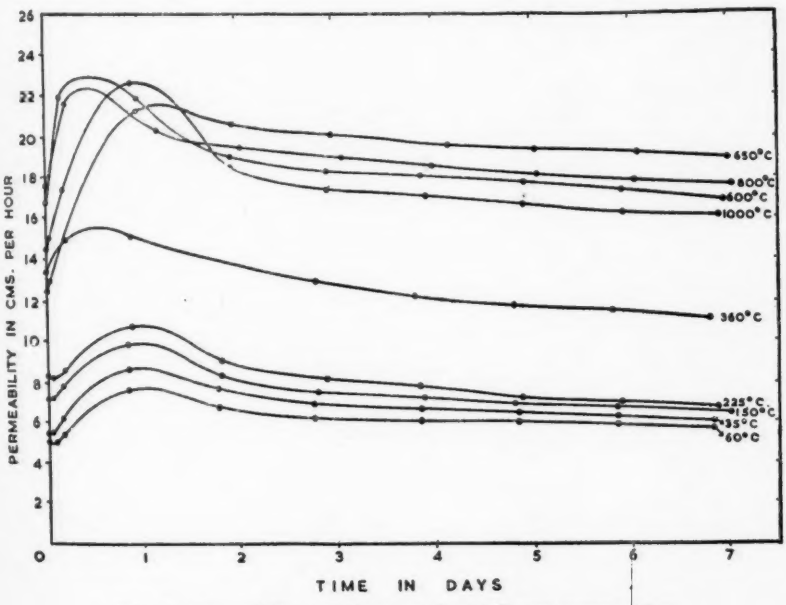


FIG. 3. Permeability of soils Heated at different temperatures.

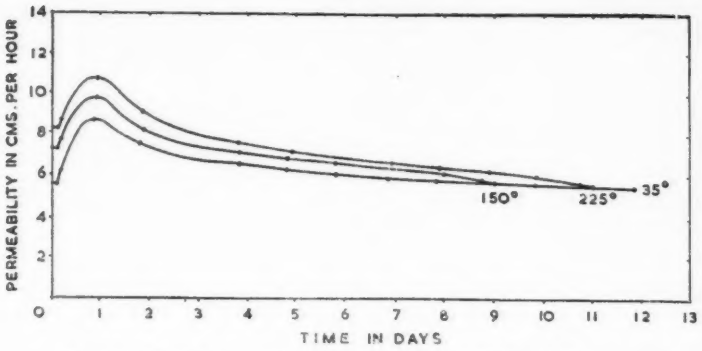
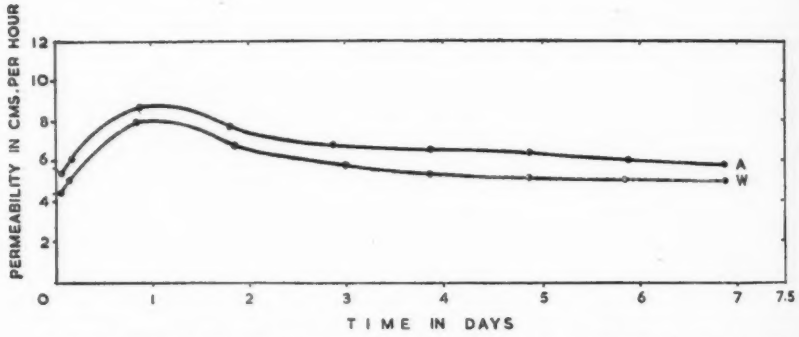


FIG. 4. Final Permeability of Soils Heated at Different Temperatures.



A : PERMEABILITY OF NORMAL SOIL KEPT EXPOSED TO ROOM TEMPERATURE IN AUTUMN.

W : PERMEABILITY OF NORMAL SOIL KEPT EXPOSED TO ROOM TEMPERATURE IN WINTER.

FIG. 5

flowing liquid and that the temperature coefficient of the viscosity of water is of the same order.

In view of the high temperature coefficient of permeability, a thermostatic chamber enclosing the permeability apparatus was found to be necessary. An air thermostat described by Vernon[11] and later adapted by Rao, K. S.[9] was constructed. The entire permeability apparatus was enclosed in the air thermostat. In all the permeability measurements, the thermostat was maintained at 35° C.

Heating of the Soil.—The soil was heated to the following temperatures: 60° C., 150° C., 225° C., 360° C., 600° C., 650° C., 800° C., and 1,000° C. For 60° C. and 150° C. an electrical hot air oven was used and for higher temperatures an electric furnace was employed. The temperature could be controlled to an accuracy of $\pm$ 5° C. The soil was kept at each of these temperature over an interval of 3½ hours. After heating, the soil was removed into a glass stoppered bottle and kept in a desiccator overnight. On the next day, the soil sample was taken out for permeability study. Ordinarily an interval of about 16 to 20 hours was allowed between the heating and permeability measurement. This procedure was common to all the soil samples heated to different temperatures.

Soil Grain Size in Relation to Permeability.—Earlier workers have uniformly employed soil samples passing through 2 mm. sieve in their permeability studies. Fireman[7] has discussed the choice of grain size for permeability measurements and has indicated that 1 mm. sieve sample is better than 2 mm. sieve samples.

In our present study, considerable non-reproducibility was noticed between two samples of the same soil at the same temperature, when 2 mm. standard was adopted. By adopting 1 mm. standard there was an improvement. Therefore in all the experiments 1 mm. sieve sample was employed.

Mode of Packing of the Soil.—Mode of packing affects the porosity of the soil and consequently its permeability. Fireman[7] has reported that with the increase in the number of impacts on the soil, the permeability decreases. Earlier workers have all uniformly adopted 10 impacts through a height of 2·5 cm. as the standard in packing. The same standard was employed in the present work.

Discussion

The results of permeability measurements have been presented in Figs. 2, 3, 4 and 5. Each curve is the selection made out of three or more experiments. Such a repetition of the experiments was found to be necessary in view of the fact that very high order of reproducibility is not possible in the permeability measurements.

Reproducibility of Permeability Measurements.—Permeability of a soil is dependent upon its porosity. The porosity depends upon the particle size and the mode of packing. As these factors are variable over a wide range, it was found necessary to determine the accuracy with which permeability measurements could be reproduced under controlled conditions of the above variable factors.

With the standardised procedure of filling and packing the soil as described above, experiments were carried out on two samples of the normal soil. The permeability data have been presented in Fig. 2. The difference in permeabilities of the two samples is not more than 0·2 cm. per hour and the difference over the entire period of experiment is not found to exceed this value. The accuracy of $\pm$ 0·2 cm. per hour is fairly good, in view of the difficulty encountered in maintaining reproducibility of packing.

Variations in Permeability with Time under Prolonged Submergence of Soil in Water.—The behaviour of soils in regard to permeability changes with time under conditions of prolonged submergence of soil in water has been reported by earlier workers.[1, 4, 5]

With the usual mode of wetting the soil by dropping water from above, all soils show a common behaviour. The permeability-time curves are S-shaped. There are three distinct phases in the curve. There is an initial decrease in permeability. After the attainment of a minimum, there is an increase reaching a maximum. Finally the permeability falls off gradually and continuously. These changes have been explained as being due to different causes. The initial fall in permeability is attributed to the removal of the bivalent ions and the swelling of the soil. These changes reduce the size of the pores and consequently there is a fall in the permeability.

In the second phase the increase in permeability is due to the removal of air entrapped in the soil. According to the usual mode of wetting the soil, certain amount of air is always entrapped in the pore space of the soil. The removal of this entrapped air is brought about by the solvent action of water for air. With the removal of the air, the pores are free to allow the passage of water and thus the permeability goes on increasing.

After the complete removal of the entrapped air, the third phase sets in, in which there is decrease in permeability. This decrease is continuous and gradual and lasts over several months and probably even years. This continuous fall in permeability in the third phase has been attributed to the decrease in porosity and sealing of the soil brought about by the disintegration of the soil aggregates and also the microbiological activity.

The air theory of the increase in permeability in the second phase and the theory of biological clogging of soil pores in the third phase have been experimentally confirmed.[1, 6, 7]

Significance of the Initial, the Maximum and Final Permeabilities.—For purposes of comparison, it is necessary to choose any one of the above three permeabilities as a standard. The initial value is greatly influenced by the mode of packing and the maximum by the amount of air entrapped in the

course of packing. The final value, however, is free from these vitiating influences. At any time after soaking the soil with water, the final permeability indicates the stage of disintegration of the soil. Therefore, these final values can be taken as the standard for purpose of comparison. With soils, which differ widely in their composition, such procedure may be open to objection. But in the present case, in which the soil is the same and the effect of heating the same soil on permeability is studied, the above procedure is justifiable.

Effect of the Temperature of Heating of the Soil on Permeability.—The soils heated to the different temperatures, *i.e.*, 60° C., 150° C., 225° C., 360° C., 650° C., 800° C. and 1,000° C. have shown differences in their behaviour retaining, however, the general characteristics of the permeability changes of a normal soil (Fig. 3). The permeability studies in all these cases were extended upto a period of one week. At the end of this period the curves did not indicate any new change, excepting a slow and continuous decrease. The permeability-time curve of the various soils were running practically parallel to one another and therefore the study was discontinued.

For purposes of comparison the final permeabilities of soils at the end of one week's submergence in water have been chosen.

Heating of Soil to 60° C. *and Soil Shrinkage.*—The soil heated to 60° C. shows a lower permeability than the normal soil throughout the entire period of study (7 days). The initial permeability is lower by 0·5 cm. per hour whereas the maximum is lower by about 1 cm. per hour and the final permeability by 0·5 cm. per hour. This small decrease in permeability is probably due to a shrinkage of the soil structure brought about by heating. This shrinkage results in a reduction of the porosity and consequently in permeability. The temperature of 60° C. is not too high and obviously it has not brought about any drastic changes in the soil excepting this shrinkage.

Heating of Soil to Higher Temperatures upto 650° *C. and Soil Aggregation.*—The soils heated to higher temperature of 150° C., 225° C., 360° C., 600° C., 650° C., 800° C. and 1,000° C. have all shown increase in permeability in all the three stages, *i.e.*, the initial value, the maximum and the final permeability. For instance in the case of soils heated to 150° C., 225° C., 360° C., 600° C. and 650° C., the increase has been progressive. This progressive increase in permeability is obviously connected with changes in porosity of the soil.

Schumacher has tried to divide the total pore space in a soil into capillary (finer pores) and non-capillary (wider pores) porosity. Of these the latter is mainly responsible for permeability. The variation of total porosity as well

as the corresponding variation in capillary and non-capillary porosities with a change in the size of the soil particles has been indicated.[2] As the particle size decreases from 5 mm. to 0·5 mm., the total porosity falls by about 24% whereas the non-capillary porosity falls by nearly 93%. There is correspondingly, a decrease in permeability of such a system. From the above it is clear that permeability property is dependent essentially on the wider pores (non-capillary porosity).

From 150° C. and above, the soil has shown a marked increase in permeability. Referring to the final permeability values, we notice that the soil heated to 150° C. has a permeability of 6·5 cm. per hour and soils heated to 225° C., 360° C., 600° C. and 650° C. have permeabilities of 6·8 cm., 11·0 cm., 16·8 cm. and 19·0 cm. per hour. The permeability of soil heated to 650° C. is nearly 3 times that of soil heated to 150° C. and about 3½ times that of the normal soil. The final permeability of normal soil is 5·5 cm. per hour. Such a big increase in permeability indicates a corresponding increase in wider porosity.

Increase in wider pores can be postulated by an increase in the size of the soil particles. It follows that higher temperatures bring about drastic structural changes resulting in the aggregation of smaller particles into bigger particles. It is only by such a mechanism of the aggregation of soil particles that increase in the wider porosity can be accounted for and consequently an increase in permeability.

Heating of Soil above 650° *C. and Incipient Fusion.*—At temperatures higher than 650° C., the soil has shown a fall in permeability. For instance, soil heated to 800° C. has suffered a decrease in permeability by 1·5 cm. per hour and the soil heated to 1,000° C. by 3·0 cm. per hour from that of 650° C. The permeability-time curves also show certain amount of overlapping in the initial stages. Several experiments were tried at each one of these temperatures. Slight divergence was always noticeable in the permeability values of the different experiments at the same temperature. The reproducibility is less accurate. Nevertheless, the existence of a definite decrease in the final permeabilities of soils heated to temperatures above 650° C., indicates a decrease in porosity which is most probably brought about by incipient fusion of the soil particle at high temperatures.

There is another prominent difference noticeable in the general feature of the curves. The permeability-time curves for temperatures upto 225° C. have all shown an initial decrease whereas for higher temperatures the soil shows no initial decrease. On the other hand, it steadily increases from the very beginning. The absence of the initial decrease indicates the absence

of swelling. Obviously, intensive heating to high temperatures has destroyed the swelling property of the soil.

From the foregoing discussion, it follows that low temperatures like 60° C. bring about only the shrinkage of the soil reducing the porosity, whereas high temperatures upto 650° C. bring about the aggregation of smaller soil particles into bigger particles. Above 650° C. the soil seems to suffer an incipient fusion resulting in a decrease of porosity.

Final Permeability of the Soil Under Prolonged Submergence in Water.— After the initial and the maximum permeabilities, a soil shows a steady fall in permeability. The final value goes on continuously decreasing over several days, months and probably even years. The normal soil at room temperature has been studied upto 12 days and has shown a steady decrease in the final value. The final permeabilities of soils heated to 150° C. and 225° C. have been followed and they have been found to coincide with those of the normal soil after the ninth and eleventh day respectively (Fig. 4). It is just probable that the permeabilities of soils heated to higher temperatures, though far higher, may after a very long period (probably years if not months) coincide with that of the normal soil owing to slow and continuous disintegration.

Degree of Saturation of Air in Water and its Influence on Permeability.— The increase in permeability to a maximum in the second phase of the permeability-time curve is based on the entrapped air theory. The rate of the increase of the permeability and magnitude of the maximum obviously depend upon the degree of saturation of air in water. Ordinarily distilled water will not have reached saturation as the solubility and the rate of dissolution of air are very low unless water is kept exposed to air for a very long period. Therefore the air entrapped in the soil is removed by the percolating unsaturated water.

With the onset of winter, as the present work was proceeding an interesting experimental difficulty was incidentally noticed in connection with the degree of saturation of air in water. The temperature of the thermostat was maintained at 35° C. throughout the measurements, whereas the distilled water of the reservoir which was kept outside the thermostat was at about 20° C. This water, nearly saturated with air was preheated to 35° C. by passing it through a copper coil kept in a water-bath inside the thermostat. After this preheating the water was passed through the permeameter tubes. On the second or the third day, accumulation of air bubbles on the top layers of the soil was noticeable. These bubbles were found gradually to grow in size and the accumulation tended to extend to lower layers. The

net result was that the soil was bulging and was being puffed up and this obviously destroyed the original structure of the soil. Consequently the permeability measurements were vitiated. In fact the permeability-time curve followed a zigzag path rather than a smooth course.

The cause of this puffiness is the accumulation of air. This air is released from the percolating water. The distilled water in the reservoir which is nearly saturated with air at the room temperature of about 20° C. is raised to 35° C. when it enters the thermostat. Owing to decreased solubility of air in water at high temperatures, normally the excess air should have been released from solution but actually this excess air is held in water in supersaturated condition. The supersaturation is released only when the supersaturated water comes into contact with the soil and consequently the excess air is released on the soil surface and this accumulates in the intergranular spaces. The soil is thus puffed up. The phenomenon of super-saturation in solutions is well known. It is generally recognised as a metastable state and the release of the supersaturation is ordinarily brought about by the introduction of surface or nucleii. It is probable that in the present case, the surface of the soil facilitates the release of supersaturation of air in water.

In order to eliminate this experimental difficulty and to have the distilled water in a fairly unsaturated condition before it is introduced into the soil, the following procedure was adopted.

The distilled water at the room temperature of 20° C., was passed through a tower packed with silica gel and maintained at 45° C. The water was next passed through the copper coil kept in a water-bath inside the thermostat. The heating of the tower was effected electrically by winding the tower with nichrome wire. The silica gel enabled the release of supersaturation. The released air was allowed to accumulate in a trap in order to avoid the possibility of air blocking the water channel. The water saturated with air at 45° C. when reduced to 35° C. would be fairly unsaturated. After this treatment the puffing of the soil was no longer noticeable. The degree of unsaturation of air in water was controlled by controlling the temperature of the silica gel tower. For instance, when the tower was kept at 45° C., the permeability-time curve obtained with the normal soil was almost identical in shape as the curve obtained in an earlier experiment, carried out in summer when this supersaturation releasing device was not necessary (Fig. 5).

Seasonal Variations in Water Content, Permeability and Porosity of Soil.—The air-dry soil which constituted the main stock was stored in a box kept exposed to air in the laboratory. A sample of the soil was taken out

for permeability measurements in the month of September (beginning of autumn). The permeability-time curve is shown in Fig. 5. Another sample of the same soil was again experimented upon in December (beginning of winter) in connection with the study of the degree of saturation of air in water and its effect on permeability (Fig. 5). The two curves are shown side by side and afford an interesting comparison. The soil sample of winter has lower permeabilities than the sample of autumn over the entire period of permeability study (7 days). The experiment on the winter soil was originally planned as a control to have an idea of the degree of saturation of air in distilled water. Incidentally, this seasonal difference in permeability was noticed. This difference was confirmed by further experiments on samples of the same soil.

The water content of the winter soil was determined and it was found to be 1·12% whereas the water content of the same soil in autumn was 1·54%.

The decrease in permeability of the soil indicates a decrease in porosity. It follows that with the change of season from autumn to winter, the soil has suffered a shrinkage. This shrinkage is due to the loss of water by nearly 0·42%. The loss of water itself is governed by a fall in humidity of the air with the change of season. That there is a fall in humidity with the change of season from autumn to winter is obvious from the following weather data which were kindly supplied by the Meteorological Department, Government of India, New Delhi. The average daily relative humidity in the month of September is 59% whereas in December it is 49%. The average daily temperatures for these months are 29·2° C. and 15·2° C. respectively. The above are the average of weather data in Delhi during the past 60 years.

These seasonal changes of shrinkage and swelling of the soil accompanied by the changes in atmospheric temperature and humidity are very interesting indeed, and probably have an important bearing in soil engineering.

Summary

Permeability studies have been carried out with the Gangetic alluvial soil of Delhi (India).

The soil was heated to the temperatures of 60° C., 150° C., 225° C., 360° C., 600° C., 650° C., 800° C. and 1,000° C. The heated soil was subjected to permeability measurements.

On heating the normal soil to 60° C. the permeability decreased indicating a decrease in porosity. This decreased porosity suggests a shrinkage in soil structure. From 60° C. to 650° C., the soil shows a progressive

increase in permeability. This indicates that in this temperature range, the soil suffers a drastic structural change. The smaller soil particles grow into bigger ones and this results in the increase of wider pores. These wider pores account for increased permeability. Above 650° C., the soil suffers a fall in permeability. This indicates a decrease in soil porosity which is probably brought about by incipient fusion of the soil particles at high temperatures.

The general trend of the final permeabilities of soils heated to different temperatures seems to be to revert to that of the normal soil. Soil heated to 150° C. reverted to the permeability of normal soil after 9 days and that of the soil heated to 225° C. after 11 days.

When water supersaturated with air is passed through a soil, the soil is puffed up owing to the release of supersaturation and accumulation of air bubbles in the intergranular space of the soil.

The soil suffers a loss in water and permeability with the change of season from autumn to winter. This seasonal variation indicates that a soil shows shrinkage in the low humid atmosphere of winter and swelling in the high humid atmosphere of autumn.

The authors are grateful to Dr. D. S. Kothari, Scientific Adviser to the Ministry of Defence, Government of India, New Delhi, for evincing keen interest in the work and kindly permitting the publication of the paper.

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NAPHTHOQUINONE SERIES—PART I

Brazanquinone Vat Dyes from 2 : 3-Dichloro-1 : 4-Naphthoquinone : Part I Constitution of "*iso*-Dinaphthalene Oxide"

By B. Suryanarayana and B. D. Tilak, F.A.Sc.

(*Department of Chemical Technology, University of Bombay, Bombay* 19)

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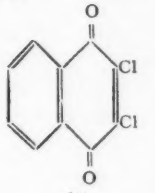
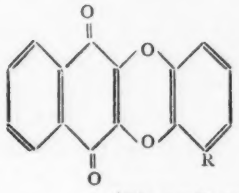
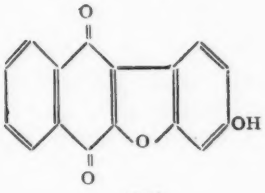
2: 3-Dichloro-1 : 4-naphthoquinone (I) is marketed in U.S.A. under the name " Phygon " for use as an agricultural fungicide[1] and as an anti-mildew agent[1] for textiles. Of the several methods suggested for the preparation of (I), a convenient laboratory method[2] consists in sulphonation of α-naphthol followed by treatment of the diluted sulphonation mixture with potassium chlorate and hydrochloric acid. The chlorine atoms in (I) being reactive and easily replaceable, a series of 3-chloro-2-substituted, 2: 3-disubstituted and polycyclic derivatives of 1 : 4-naphthoquinone have been synthesized starting from (I).



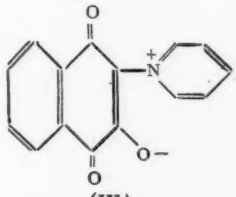
(I)



(II), R=H or OH



(III)

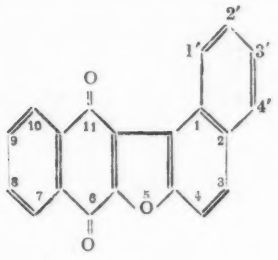


(IV)

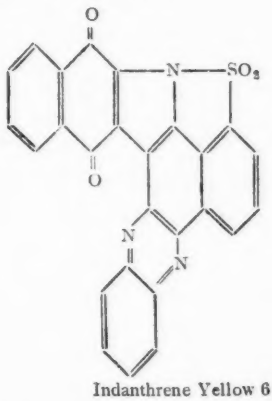
Both the chlorine atoms are replaced by condensation with phenol[2] in presence of sodium ethoxide to give 2: 3-diphenoxy-1 : 4-naphthoquinone. It has now been observed that the diphenoxy derivative is also formed by condensation of (I) with phenol in pyridine. The chlorine atoms, likewise, react with the adjacent hydroxyl groups in catechol[2] and pyrogallol[3] leading to dioxine derivatives such as (II), although the structure assigned for the condensation product with pyrogallol needs further confirmation. With

resorcinol,[4] however, one of the chlorine atoms in (I) reacts with one hydroxyl group and the other removes the hydrogen atom from the reactive 4-position which is *o*-, *p*- to the hydroxyl groups in resorcinol, leading to the furan derivative, 3-hydroxy-6:11-brazanquinone* (III). The above condensation was carried out by Graebe and Liebermann[5] in sodium ethoxide, but Eistert[6] has reported that the reaction may also be carried out in pyridine. It has, however, been noted by us that reaction in pyridine gives a very impure product from which only a small amount of (III) can be isolated, the major product formed being the betaine (IV). The formation of the betaine by the reaction of (I) with pyridine was first described by Ullmann and Ettisch[2] and the compound was later constituted as (IV) by Eistert.[6]

Eistert[6] has studied the use of (I) as an intermediate for the synthesis of vat dyes. Condensation of (I) with phenols containing a *meta*-substituent such as a hydroxy, amino, alkyl or aryl amino group gives 3-substituted brazanquinones. Reaction with β-naphthol gives 1:2-benzobrazanquinone (V). 1-Phenyl-3-methyl-5-pyrazolone and "4-hydroxy-1-methyl-2-picolone" react with (I) presumably in their enolic forms leading to complex dark-coloured furan derivatives. Thioindoxyl likewise gives a furanothionaphthenonaphthoquinone derivative. The colour of these heterocyclic derivatives of furanonaphthoquinones was explained by Eistert on the basis of resonance between different betaine or meso-ionic structures. The above naphthoquinone derivatives prepared by Eistert vatted in alkaline hydrosulphite solution but had poor substantivity to cotton.



(V)



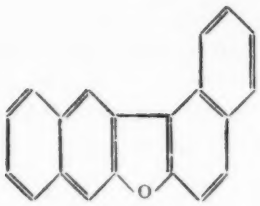
Indanthrene Yellow 6 GD

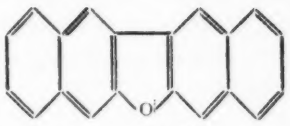
* 2:3–Benzo-4:5–(2′ :3′–naphtho) furan is referred to as "brazan" in the literature from its derivation from brazilin.[4] 2:3 (2′ :3′–Coumarano)-1:4–naphthoquinone is described as "brazanquinone". The trivial name "brazanquinone" has been used in this paper in common with other workers.

Indanthrene Yellow 6 GD,[7] a greenish yellow dye, is of interest as it is free from photochemical tendering activity and appears to be the only example of a commercial naphthoquinone vat dye. It is prepared by the condensation of (I) with the azine obtained by the reaction of the nitroso derivative of naphthasultam with *o*-phenylenediamine.

Substantive vat dyes have now been prepared by the reaction of (I) with bromo derivatives of α- and β-naphthols and by condensation of (I) with 2-hydroxy-3-naphthanilide (Naphtol AS). It has been mentioned earlier that condensation of (I) with phenol in sodium ethoxide or pyridine gives 2:3-diphenoxy-1 : 4-naphthoquinone. Similar condensation of β-naphthol would therefore lead to either 1:2-di(β-naphthoxy)-1 : 4-naphthoquinone or to 1:2-benzobrazanquinone (V). In view of the fact that resorcinol gives the furan derivative, 3-hydroxybrazanquinone and also in view of the reactivity of the α-position in β-naphthol, it appears that the condensation product of (I) with β-naphthol is more likely to be constituted as (V) rather than the dinaphthoxy derivative. However, since the two compounds have nearly the same elementary composition, it is necessary to provide unambiguous proof as regards the furan structure (V) of the condensation product (A) obtained by the reaction of (I) and β-naphthol in pyridine. It is also a curious fact that the furan and the dinaphthoxy structures derived from (I) and Naphthol AS have also very nearly the same elementary composition.

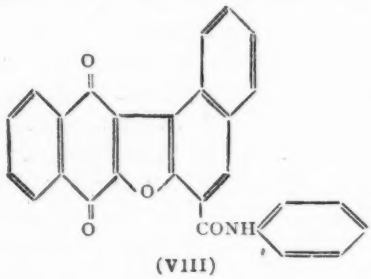
"*iso*Dinaphthalene Oxide" (B), a dinaphthofuran obtained by prolonged heating of β-naphthol with alkali-earth oxides above 280°, was constituted by Clemo and Spence[8] as dinaphtho (2′ : 3′ : 2 : 3-) (1″ : 2″ : 4 : 5) furan (VI) in preference to the alternative linear structure (VII) on the basis of spectroscopic data[9] and its oxidation to a *p*-monoquinone. Since the condensation product (A) of (I) and β-naphthol in pyridine was identical with the quinone prepared from (B) by oxidation, Eistert[6] concluded that (A) is 1:2-benzobrazanquinone (V). However as the constitution of (B) itself is not unambiguously proved, the constitution of (A) suggested by Eistert[6] cannot, therefore, be regarded as settled. Buu-Hoï[10] has recently claimed to have provided proof in confirmation of Clemo and Spence's assumption by the synthesis of (B) by the zinc dust distillation of (A) and by demonstrating that "1-substituted-2-naphthols (for example, 1-methyl-2-naphthol)" do not give furan derivatives by reaction with (I). The latter observation shows that β-naphthol links with (I) in the 1- and not the 3-position. Buu-Hoï has, however, not described the product actually obtained in the reaction between (I) and a 1-substituted 2-naphthol.


(VI)

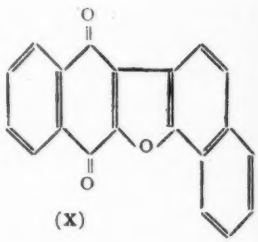

(VII)

More positive evidence as regards the constitution of (A) has now been obtained by studying the reaction of (I) with 1-bromo-2-naphthol in pyridine. The latter reaction gave a halogen-containing brownish-orange quinonoid reaction product together with a halogen-free substance which proved to be identical with (A). The 1-position in β-naphthol is thus involved in the reaction of β-naphthol with (I) and (A) is therefore constituted as the furan derivative, 1 : 2-benzobrazanquinone (V). The constitution of "*iso*dinaphthalene oxide" as dinaphtho (2′ : 3′ : 2 : 3) (1″ : 2″ : 4 : 5) furan (VI) follows from its conversion to (V) by oxidation[6] and conversely by its synthesis from (V) by zinc dust distillation.[10]

Condensation of (I) (1 mole) with 1-bromo-2-hydroxy-3-naphthanilide[11] (1 mole) in pyridine gave a halogen-containing quinonoid compound. Using two moles of the bromo derivative a halogen-free substance was obtained which proved to be identical with the condensation product of Naphthol AS and (I) in pyridine. The 1-position in Naphtol AS is therefore involved in the reaction with (I) and the resulting condensation product is unambiguously constituted as the furan structure, 1 : 2-benzobrazanquinone- 4-carboxyanilide (VIII) and not as a 2 : 3-dinaphthoxynaphtho-



(VIII)



(X)

quinone. The constitution of the halogen-containing quinones obtained by the condensation of (I) with 1-bromo-2-naphthol and 1-bromo-2-hydroxy-3-naphthanilide is under investigation. The condensation products obtained

from (I) and compounds of the Naphtol AS series[12] have likewise been constituted as brazanquinone derivatives such as (VIII) where both the hydroxy group and the coupling position in the naphthol are involved.

To study the effect of the introduction of a bromine atom in (V), 6-bromo-2-naphthol was condensed with (I) to give 3′-bromo-1 : 2-benzobrazanquinone (IX). The latter proved to be much more substantive than (V). Buu Hoï[10] has recently claimed to have prepared (IX), but the product obtained by him is impure as it melts much lower than the product described in the present paper. It is probable that the dye obtained by Buu Hoï is contaminated with the betaine (IV) which is also formed together with (IX).

3 : 4-Benzobrazanquinone[13] (X), prepared by condensation of (I) with α-naphthol, is also weakly substantive to cotton although it is slightly more substantive as compared to (V). Reaction of 4-bromo-1-naphthol with (I) gave 2-bromo-3 : 4-benzobrazanquinone (XI) which had good substantivity and gave a bright yellow shade on cotton. The increase in substantivity by the introduction of a bromine atom in (X) was greater as compared to the increase in substantivity observed when bromine was introduced in (V). 4-Bromo-1-naphthol was obtained in a purer form (m.p. 128°) and in better yields (55%) by a modification of the method due to Fieser and Desreux[14] who have reported 23% yield of the bromo derivative, m.p. 120°.

The condensation of (I) with Naphtol AS was first carried out in presence of sodium ethoxide and alcohol. The resulting bright yellow dye (VIII) (m.p. 315–19°) has good fastness properties and possessed better substantivity to cotton than several brazanquinone vat dyes obtained from more substantive Naphthols.[12] Since a small amount of 2-chloro-3-hydroxy-1 : 4-naphthoquinone was formed in this reaction and as the yield of (VIII) was only 62%, suitability of other media for this reaction was studied. Reaction in toluene in presence of potassium carbonate as an acid-binding agent was unsuccessful. Condensation in diethylaniline gave poor yields (28·5%) of (VIII), (m.p. 312-15°). However when pyridine was used as the solvent, (VIII) was obtained in pure crystalline form but the yields were again not satisfactory (m.p. 315°; yield 41·9%) on account of the conversion of (I) to the betaine (IV). This drawback was overcome by carrying out the reaction in dry toluene using enough pyridine to react with the hydrochloric acid liberated in the reaction. This method led to higher yields (72–75%), but the product gave lower m.p. 294–97°, whereas the product obtained when pyridine was used as the solvent melted at 315°. In the above condensation pyridine may be substituted by diethylaniline but the yield of (VIII) was lowered. In the light of these experiments, pyridine was used in subsequent condensations of (I) with compounds of the Naphtol AS series.[12]

EXPERIMENTAL

Condensation of 2 : 3-*dichloro*-1 : 4-*naphthoquinone* (*I*) *with* 1-*bromo*-2-*naphthol*

2 : 3-Dichloro-1 : 4-naphthoquinone (I) (2·27 g.) was added to a boiling solution of 1-bromo-2-naphthol (4·5 g.) in pyridine (20 c.c.). The dark brown reaction mixture was heated under reflux for 2½ hours and then cooled. On leaving it overnight at 0°, lustrous brown crystalline compound (1·1 g.), m.p. 243–46°, separated. The product was repeatedly extracted with boiling water to remove the betaine (III). The residue, m.p. 265–66°, crystallized from glacial acetic acid in brownish yellow needles (0·2 g.), m.p. 269°. The product was free from halogens and nitrogen and was found to be identical with 1 : 2-benzobrazanquinone (V). The aqueous extracts on concentration gave the betaine (0·5 g.).

The pyridine mother-liquor on dilution with alcohol (50 c.c.), gave a halogen-containing orange-brown residue (1·0 g.), m.p. 237–43°, which was collected, washed with alcohol and purified by extraction with boiling water as before. The betaine-free product (0·65 g., m.p. 237–39°) after 4 crystallizations from xylene gave brownish orange rectangular plates, m.p. 255·5–56° (Found: C, 67·0; H, 3·3; Cl, 13·5%). When tested according to Vogel[15] the compound was found to contain chlorine, but not bromine.

The pyridine-alcohol filtrate, after removal of the above product, was concentrated to a small bulk and poured into ice and hydrochloric acid when a tarry product separated. The mixture was filtered through cotton-wool and the tarry residue was repeatedly extracted with boiling water. The aqueous extracts on concentration and cooling gave the betaine (0·5 g.). The water-insoluble residue was dissolved in 10% sodium hydroxide, treated with Norit and filtered. The alkaline solution was saturated with carbon dioxide and allowed to stand. Fine colourless needles (2·0 g.), m.p. 70–75°, separated which were found to be identical with 1-bromo-2-naphthol.

Condensation of 2 : 3-*dichloro*-1 : 4-*naphthoquinone* (*I*) *with* 1-*bromo*-2-*hydroxy*-3-*naphthanilide*

Method A.—Compound (I) (1·1 g., 1 mol.) was added to a boiling solution of 1-bromo-2-hydroxy-3-naphthanilide (1·7 g., 1 mol.) in pyridine (25 c.c.). The yellow colour of the naphthol solution in pyridine after addition of (I) quickly changed to light green → bright green → dark green and finally to brown. The mixture was heated under reflux for 3 hours and left overnight at 0°. The yellow crystalline product (0·3 g.) which separated was washed with alcohol and recrystallized from pyridine when it gave yellow needles, m.p. 284–85°. The mother-liquor on further standing

gave a second crop of the yellow product (0·8 g.), m.p. 265–70°. After removal of the betaine (II) by extraction with boiling water, the latter gave a residue (0·7 g.), m.p. 283–84°, which was identical with the first crop. After three recrystallizations from xylene it gave yellow clusters of needles, m.p. 283–85° (Found: C, 66·6; H, 3·0; Cl, 9·7; N, 2·85%). The compound when tested according to Vogel[15] showed the presence of chlorine but not bromine.

The pyridine mother-liquor, after separation of the above product, was added to ice and hydrochloric acid. The tarry product which separated gave 0·2 g. of the betaine (IV) on extraction with boiling water. The water-insoluble residue was dissolved in alkali and the alkaline solution was clarified with Norit. Saturation of the clarified alkaline solution with carbon dioxide, gave 1-bromo-2-hydroxy-3-naphthanilide (0·2 g.).

Method B.—The above reaction was repeated using (I) (2·27 g., 1 mol.), 1-bromo-2-hydroxy-3-naphthanilide (6·9 g., 2 mols.) and pyridine (60 c.c.). The brown reaction mixture was refluxed for 3 hours and then cooled. The yellow product (0·8 g., m.p. 283–87°) which separated was collected and crystallized from xylene (200 c.c.) when it gave yellow needles, m.p. 290–97°, containing traces of halogens. Recrystallization from nitrobenzene gave a product melting at 295–99°. Repeated crystallization of this product from pyridine gave a halogen-free product, m.p. 315–16° which was identical with 1:2-benzobrazanquinone-4-carboxyanilide (VIII).

3:4-*Benzobrazanquinone* (*X*)

α-Naphthol (0·7 g.) and (I) (1·1 g.) were refluxed with pyridine (15 c.c.) for 3 hours. The dark brown reaction mixture was cooled in ice and the crystals which separated were collected, washed with alcohol and dried (0·9 g., yield 60%), m.p. 229–30°. Recrystallization from benzene-alcohol (1:1) gave yellow flat needles, m.p. 234° (Fieser and Brown[13] give m.p. 229–30°) (Found: C, 80·2; H, 3·6. Calc. for $C_{20}H_{10}O_3$: C, 80·5; H, 3·4%). The mother-liquor was added to concentrated hydrochloric acid (20 c.c.) and crushed ice (25 g.). The orange-yellow product (0·35 g.), m.p. 280–85°, which separated was found to be the betaine (IV).

4-*Bromo*-1-*naphthol*

Iodine (26 g.) was dissolved in a solution of bromine (5 c.c.) in glacial acetic acid (60 c.c.) by warming to 50°, under continuous agitation. The solution of iodine bromide was added dropwise to a solution of α-naphthol (14 g.) in acetic acid (45 c.c.) in 15 minutes. The mixture was cooled externally with ice and connected to a water pump during the addition. After one

hour during which the flask was shaken occasionally, the mixture was poured gradually into a vigorously stirred solution of sodium bisulphite (18 g.) in water (700 c.c.) when most of the bromo derivative precipitated. The mixture was neutralized with sodium bicarbonate (160 g.) which was added cautiously during 1½ hours under continued agitation. The precipitate was collected, washed with water and dried (17·5 g.). Crystallization from 33% aqueous alcohol (800 c.c.) gave pale pink long needles, m.p. 128° (12 g., yield 55%). Fieser and Desreux[14] have reported 23% yield of the crystalline compound melting at 120°.

2-Bromo-3 : 4-benzobrazanquinone (XI)

A mixture of 4-bromo-1-naphthol (2·2 g.), (I) (2·2 g.) and pyridine (20 c.c.) was refluxed for 3 hours. The golden yellow crystals which separated on cooling were collected, washed with alcohol and extracted with boiling water to remove the betaine. The product (1·5 g.), m.p. 269°, after three recrystallizations from benzene, gave yellow needles, m.p. 270–71° (Found: C, 63·8; H, 2·7. $C_{20}H_9BrO_3$ requires C, 63·7; H, 2·4%). Concentration of the mother-liquor gave a further crop of the product (0·1 g.). Evaporation of the alcohol washings and the aqueous extracts gave the betaine (IV) (1·0 g.).

3′-Bromo-1 : 2-benzobrazanquinone (IX)

6-Bromo-2-naphthol[16] (2·24 g.), (I) (2·27 g.) and pyridine (20 c.c.) were heated under reflux for 3 hours. The brown residue which separated on cooling in ice was collected, washed with alcohol and dried (2·25 g.), m.p. 275–80°. After repeated extraction with boiling water, lustrous brown plates (0·85 g.), m.p. 317–18°, were obtained as residue. Recrystallization from xylene gave lustrous orange yellow plates, m.p. 324° (Buu Hoï[10] quotes m.p. 308°) (Found: C, 63·9; H, 2·6. $C_{20}H_9BrO_3$ requires C, 63·7; H, 2·4%).

1 : 2-Benzobrazanquinone-4-carboxyanilide (VIII)

Condensation in Presence of Sodium Ethoxide.—Sodium (0·23 g.; was dissolved in absolute alcohol (50 c.c.) and Naphtol AS (2·6 g.) was added. The solution was heated to boil and a suspension of (I) (1·1 g.) in absolute alcohol (150 c.c.) was then added. The mixture was initially greenish yellow but soon turned dark yellow and yellow crystals started separating out. After refluxing for 3 hours, the mixture was cooled and filtered. The bright yellow crystalline residue was washed with hot water to remove sodium chloride and dried (1·3 g., yield 62%), m.p. 315–19°. It crystallized from pyridine in felted needles, m.p. 316° (Found: C, 77·8) H, 3·3; N, 3·9. $C_{27}H_{15}NO_4$ requires C, 77·7; H, 3·6; N, 3·4%).

The alcoholic mother-liquor, on concentrating to 20 c.c. and neutralizing with conc. hydrochloric acid, gave unreacted Naphtol AS (1·7 g.), m.p. 238°. The filtrate on dilution with water gave 2-chloro-3-hydroxy-1 : 4-naphthoquinone (0·2 g.).

Condensation in Diethylaniline.—Naphtol AS (1·3 g.), (I) (1·1 g.) and diethylaniline (15 c.c.) were refluxed for 2 hours and then cooled. The yellow needles which separated were collected, washed with alcohol and dried (0·6 g.), m.p. 312–15° (yield 28·5%). Mixed m.p. with the product obtained in the above experiment was not depressed.

Condensation in Pyridine.—Naphtol AS (5·3 g.), (I) (4·5 g.) and pyridine (50 c.c.) were refluxed for 3 hours and cooled. The yellow felted needles obtained were washed with alcohol and dried (3·5 g.), m.p. 315°; raised to 316° by recrystallization from pyridine. The product was purer than the products obtained by the above methods.

Condensation in Toluene and Pyridine.—Finely powdered sample of (I) (2·25 g.) and Naphtol AS (2·63 g.) and dry toluene (150 c.c.) were heated to boil under reflux and pyridine (4 c.c.) was added dropwise in 3 hours. After refluxing for 24 hours, toluene was removed by steam distillation and the yellow residue was collected, extracted successively with boiling water, cold and then boiling 10% aqueous sodium hydroxide and finally washed with water and dried (3·05 g., yield 72·5%), m.p. 294–97°. On crystallization from pyridine, the product gave yellow felted needles, m.p. 316°.

The aqueous extracts on evaporation gave the betaine (IV) (0·15 g.). The cold alkaline extract when neutralized with acid gave the unreacted naphthol (0·25 g.) and the hot alkaline extracts gave a mixture of the naphthol and 2-chloro-3-hydroxy-1 : 4-naphthoquinone (0·8 g.).

In the above experiment if diethylaniline (3 c.c.) was used in place of pyridine, the yield of (VIII) was only 45%.

Colour Reactions and Dyeing Properties

The colour in sulphuric acid, the colour of the vats, the shades on cotton and the fastness properties of the dyes are given in Table I.

Dyes (V), (IX), (X) and (XI) give greenish blue solutions in sulphuric acid. All of them are reduced easily by alkaline hydrosulphite and are applied to cotton by the IW or the IN process. The dyes gave yellow shades of poor to moderate fastness properties.

The dye (VIII) is difficult to reduce but after precipitation from sulphuric acid it vats readily at 60–70°. It gives a bright orange yellow shade with good fastness properties.

TABLE I

Compound	Colour in sulphuric acid	Colour of the vat	Shade on cotton	Fastness		
				Light	Severe Washing	Chlorine
V	Greenish blue	Orange	Pale brownish yellow	2–3	..	..
IX	Bluish green	Red-brown	Yellow	4–5	2–3	4
X	Blue	Brownish yellow	Pale yellow	2–3	1	3
XI	Greenish blue	Orange red	Bright yellow	2–3	3	4–5
VIII	Blue	Deep red brown	Bright orange yellow	5–6	5	5

Fastness to light was found using the Atlas Fade-O-Meter and following the standards of Society of Dyers and Colourists[17] and fastness to washing and chlorine by the I.C.I. method.[18]

SUMMARY

Brazanquinone vat dyes have been prepared by the condensation of 2:3-dichloro-1:4-naphthoquinone (I) with α- and β-naphthols and their bromo derivatives and by the condensation with Naphtol AS. Reaction of 1-bromo-2-naphthol with (I) in pyridine gave a halogenonaphthoquinone together with a halogen-free naphthoquinone which proved to be identical with the reaction product (A) obtained from (I) and β-naphthol in pyridine. The 1-position in β-naphthol is thus involved in the condensation with (I) and (A) is therefore constituted as the furan derivative, 1:2-benzobrazanquinone (V). Constitution of "*iso*-dinaphthalene oxide" as dinaphtho-(2′:3′:2:3-) (1″:2″:4:5) furan (VI) follows from its conversion to (V) by oxidation and conversely by its synthesis from (V) by zinc dust distillation. The condensation product of (I) with Naphtol AS is likewise the furan derivative 1:2-brazanquinone-4-carboxyanilide (VIII) since it is also formed from 1-bromo-2-hydroxy-3-naphthanilide by loss of bromine.

Introduction of bromine in (V) and 3:4-benzobrazanquinone and the introduction of the carboxyanilide group in (V) leads to more substantive dyes. The dyes give yellow and orange yellow shades. Fastness properties of the dyes have been determined.

We are indebted to Professor Louis F. Fieser of the Harvard University, for the generous gift of 2:3-dichloro-1:4-naphthoquinone used in the present and in the subsequent work. Our thanks are also due to the Council of Scientific and Industrial Research for the award of a Fellowship to one

of us (B.S.) and to Dr. T. S. Gore for the microanalyses recorded in the paper.

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NAPHTHOQUINONE SERIES—PART II

Brazanquinone Vat Dyes from 2 : 3–Dichloro-1 : 4–Naphthoquinone : Part II

BY V. K. DIKSHIT, B. SURYANARAYANA AND B. D. TILAK, F.A.SC.

(Department of Chemical Technology, University of Bombay, Bombay 19)

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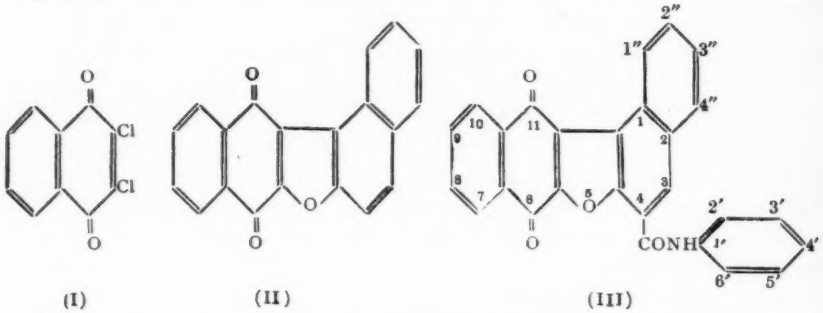
THE synthesis of brazanquinone vat dyes obtained by the condensation of 2 : 3-dichloro-1 : 4-naphthoquinone (I) with 4-bromo-1-naphthol, 6-bromo-2-naphthol and 2-hydroxy-3-naphthanilide (Naphtol AS) has been described in the previous paper.[1] The constitution of the condensation products as furan derivatives was also discussed. As against the poor substantivity of 1 : 2-benzobrazanquinone[1] (II), the 4-carboxyanilide derivative[1] (III) possessed good substantivity. The parent β-naphthol and Naphtol AS, from which



(I) (II) (III)

the above dyes were obtained, exhibit parallel substantivity to cotton, the latter being more substantive. In general the introduction of heterocyclic rings, carboxyamido groups, halogen atoms, methoxy groups and increase in structural complexity promote substantivity in the Naphtol AS series.[2] A similar study has now been undertaken in the brazanquinone vat dyes which have been prepared by the condensation of (I) with compounds of the Naphtol AS series.

Naphtol AS-E (2-hydroxy-3-naphthoic-*p*-chloranilide) is one of the highly substantive Naphtols. In order to see whether the introduction of a chlorine atom in the anilide half of (III) has a similar effect, Naphtol AS-E was condensed with (I) to give the bright yellow dye, 1 : 2-benzobrazanquinone-4-carboxy-4′-chloranilide (IV); (III) and (IV), however, had nearly the same

substantivity. The dye (III) from Naphtol AS was slightly superior in fastness to light than (IV), whereas fastness to washing and chlorine were the same. The azoic dyeings from Naphtol AS are likewise faster to light than the dyeings from Naphtol AS-E.

With a view to study the effect of the introduction of a bromine atom in the anilide and naphthalene half of (III), 2-hydroxy-3-naphthoic-*p*-bromanilide[3] and 6-bromo-2-hydroxy-3-naphthanilide[3] were condensed with (I) to give 1 : 2-benzobrazanquinone-4-carboxy-4′-bromanilide (V) and 3″-bromo-1 : 2-benzobrazanquinone-4-carboxyanilide (VI) respectively. Whereas the parent bromonaphthols gave faster azoic shades than Naphtol AS, the brazanquinone vat dyes (V) and (VI) obtained from them did not show superior substantivity or fastness properties over the bromine-free dye (III). The increase in the substantivity by the introduction of bromine in brazanquinone dyes from α- and β-naphthols[1] was, therefore, not noticeable in dyes from the bromo derivatives of Naphtol AS.

Naphtol AS-D (2-hydroxy-3-naphthoic-*o*-toluidide) has nearly the same substantivity as Naphtol AS and both give shades of nearly equal fastness. 1 : 2-Benzobrazanquinone-4-carboxy-2′-methylanilide (VII), obtained by the condensation of (I) with Naphtol AS-D, was however only weakly substantive to cotton and gave shades which were less fast than those given by (III). Introduction of a chlorine atom in the *p*-position to the anilide group in (VII) led to increase in substantivity. Thus 1 : 2-benzobrazanquinone-4-carboxy-4′-chloro-2′-methylanilide (VIII) obtained by condensation of (I) with 2-hydroxy-3-naphthoic-*p*-chloro-*o*-toluidide (Naphtol AS-TR) had good affinity to cotton and gave bright yellow shades of good fastness. Introduction of chlorine in (VII), in common with other examples where halogen atoms were introduced, did not give dyes faster to light. The inferior fastness in general of the dye (VIII) compared to (IV) indicates the unfavourable influence of the introduction of a methyl group in (IV).

2-Hydroxy-3-naphthoic-*o*-anisidide (Naphtol AS-OL), and *p*-anisidide (Naphtol AS-RL) and 2 : 5-dimethoxyanilide (Naphtol AS-BG) are more substantive than Naphtol AS and give faster azoic dyeings; the *p*-anisidide being more substantive than the *o*-anisidide and the dimethoxyanilide being more substantive than the monomethoxyanilides. Condensation of Naphtol AS-RL, Naphtol AS-OL and Naphtol AS-BG with (I) gave 1 : 2-benzobrazanquinone-4-carboxy-4′-methoxyanilide (IX), 1 : 2-benzobrazanquinone-4-carboxy-2′-methoxyanilide (X) and 1 : 2-benzobrazanquinone-4-carboxy-2′ : 5′-dimethoxyanilide (XI) respectively, but the dyes were inferior to (III) in substantivity and fastness. In the condensation of (I) with

Naphtol AS-RL and Naphtol AS-BG, alkali-soluble by-products were isolated which are probably phenols obtained by demethylation of the methoxy groups by pyridine hydrochloride formed in the reaction.[4] Attempts to isolate the hydroxy compounds in the pure form were however unsuccessful. The dye (X) had good substantivity, whereas (IX) and (XI) were less substantive. The fastness of these dyes was nearly of the same order.

Naphtol AS-BS (2-hydroxy-3-naphthoic-3′-nitranilide) is slightly more substantive than Naphtol AS but gives azoic shades of lower fastness. 1 : 2-Benzobrazanquinone-4-carboxy-3′-nitranilide (XII), obtained by condensation of Naphtol AS-BS with (I), was, however, inferior in substantivity and fastness to (III). The nitro group in (XII) is, however, reduced to the amino group during the dyeing from an alkaline hydrosulphite vat and the shade (brownish yellow) obtained from (XII) is different from the colour of (XII) in substance (red). When the dyed fibre was treated with a mixture of sodium nitrite and aqueous hydrochloric acid and then developed with an alkaline solution of β-naphtol, the shade changed to orange showing the presence of a diazotizable amino group in the dye on the fibre.

In contrast with the superior substantivity of Naphtol AS-E, AS-TR, AS-OL, AS-RL, AS-BG and AS-BS as compared with Naphtol AS, the brazanquinone vat dyes which were obtained by the condensation of these naphthols with (I) did not show higher substantivity than the parent 1 : 2-benzobrazanquinone-4-carboxyanilide (III) which was derived from Naphtol AS. The dye (III) was further found to possess the highest all-round fastness among the brazanquinone vat dyes prepared.

EXPERIMENTAL

1 : 2-*Benzobrazanquinone-4-carboxy-4′-chloranilide* (*IV*)

Naphtol AS-E (3·0 g.), (I) (2·2 g.) and pyridine (30 c.c.) were boiled under reflux for 3 hours and cooled when bright yellow needles (2·0 g.), m.p. 306–8°, separated. Recrystallization from pyridine did not raise the m.p. (Found: N, 3·3. $C_{27}H_{14}ClNO_4$ requires N, 3·1%).

1 : 2-*Benzobrazanquinone-4-carboxy-4′-bromanilide* (*V*)

2-Hydroxy-3-naphthoic-4′-bromanilide[3] (3·4 g.), (I) (2·2 g.) and dry toluene (150 c.c.) were kept boiling under reflux and pyridine (3·2 c.c., 0·04 mols.) was added dropwise during 3 hours. The mixture was refluxed for 24 hours, toluene removed by steam distillation and the residue was extracted successively with boiling water (200 c.c.) to remove betaine, boiling

5% aqueous sodium hydroxide to remove unreacted naphthol and (I) as 2-chloro-3-hydroxy-1 : 4-naphthoquinone and finally washed with water. The product (4·45 g., yield 90%), m.p. 256–58°, was recrystallized from *o*-dichlorobenzene three times when it gave orange-yellow needles, m.p. 305–6°; unaltered by further recrystallization from the same solvent (Found: N, 2·8. $C_{27}H_{14}BrNO_4$ requires N, 2·8%).

3″-*Bromo*-1 : 2-*benzobrazanquinone*-4-*carboxyanilide* (*VI*)

The condensation of (I) (2·2 g.) and 6-bromo-2-hydroxy-3-naphthoic anilide[3] (3·4 g.) was carried out as in the previous experiment and the crude product (4·4 g.), m.p. 260–65°, after three recrystallizations from xylene gave felted yellow needles, m.p. 332° (Found: N, 2·6. $C_{27}H_{14}BrNO_4$ requires N, 2·8%).

1 : 2-*Benzobrazanquinone*-4-*carboxy*-2′-*methylanilide* (*VII*)

Naphtol AS-D (2·8 g.), (I) (2·3 g.) and pyridine (30 c.c.) were heated under reflux for 3 hours and the crystalline compound, m.p. 307–10°, which separated was collected and recrystallized from pyridine when it gave bright orange felted needles, m.p. 307° (Found: C, 77·8; H, 3·2; N, 3·2. $C_{28}H_{17}NO_4$ requires C, 77·9; H, 4·0; N, 3·2%).

1 : 2-*Benzobrazanquinone*-4-*carboxy*-4′-*chloro*-2′-*methylanilide* (*VIII*)

Naphtol AS-TR (3·1 g.), (I) (2·25 g.) and pyridine (30 c.c.) were heated under reflux for 3 hours. The crystalline product (2·2 g.), m.p. 331–33°, when recrystallized from nitrobenzene, gave yellow needles, m.p. 333°; raised to 336–37° by further crystallization from pyridine (Found: N, 3·0. $C_{28}H_{16}ClNO_4$ requires N, 3·0%).

1 : 2-*Benzobrazanquinone*-4-*carboxy*-4′-*methoxyanilide* (*IX*)

Naphtol AS-RL (2·9 g.), (I) (2·2 g.) and pyridine (30 c.c.) were refluxed for 3 hours and cooled. The crystalline product (1·35 g.), m.p. 298–300°, was washed with alcohol and it gave after two recrystallizations from pyridine yellow needles, m.p. 299° (Found: C, 75·2; H, 4·0; N, 3·6. $C_{28}H_{17}NO_5$ requires C, 75·2; H, 3·8; N, 3·2%).

The pyridine mother-liquor was poured into ice and hydrochloric acid and the precipitate obtained was extracted with boiling water. The residue (1·95 g.) was dissolved in benzene and passed through a column of activated alumina. The red band at the top of the column was eluted with benzene and on concentration it gave a red compound which after recrystallization from benzene gave red needles, m.p. 255°. It was soluble in

alcoholic alkali giving a red solution which gave an orange-yellow precipitate on acidification.

1 : 2-*Benzobrazanquinone*-4-*carboxy*-2'-*methoxyanilide* (*X*)

Naphtol AS-OL (2·9 g.) and (I) (2·2 g.) were heated under reflux in pyridine (30 c.c.) and the crystalline product (1·7 g.), m.p. 300–05°, was recrystallized twice from pyridine when it gave yellow needles, m.p. 300° (Found: C, 74·6; H, 3·9; N, 3·3. $C_{28}H_{17}NO_5$ requires C, 75·1; H, 3·8; N, 3·1%).

1 : 2-*Benzobrazanquinone*-4-*carboxy*-2' : 5'-*dimethoxyanilide* (*XI*)

Naphtol AS-BG (3·2 g.), (I) (2·2 g.) and pyridine (30 c.c.) were refluxed for 4 hours, cooled and filtered. The reddish violet product (1·55 g.) was washed with alcohol, dried and crystallized from nitrobenzene four times. It gave shining violet hexagonal plates, m.p. 290–91° (Found: C, 72·6; H, 4·1; N, 3·2. $C_{29}H_{19}NO_6$ requires C, 72·9; H, 4·0; N, 2·95%).

The pyridine mother-liquor on pouring into crushed ice and hydrochloric acid gave a dark coloured precipitate which was collected, extracted with boiling water to remove the betaine and dried (1·6 g.). Since this was found to be alkali-soluble, it was extracted with 10% sodium hydroxide (50 c.c.). The extracts were treated with Norit and filtered. Carbon dioxide was then bubbled through this solution, when a red brown precipitate (1·1 g.), m.p. 230–32°, separated. Attempts to purify this substance further proved unsuccessful.

1 : 2-*Benzobrazanquinone*-4-*carboxy*-3'-*nitranilide* (*XII*)

Naphtol AS-BS (3·1 g.), (I) (2·2 g.) and pyridine (30 c.c.) were boiled under reflux for 3 hours. The orange-yellow compound (1·4 g.) obtained gave on recrystallization from quinoline orange-yellow needles, m.p. 332° (Found: N, 6·2. $C_{27}H_{14}NO_6$ requires N, 6·1%).

Colour Reactions and Dyeing Properties

The colour in sulphuric acid, the colour of the vats, the shades on cotton, and the fastness properties of the dyes are given in Table I. Fastness to light was determined using the Atlas Fade-O-Meter and following the standards of the Society of Dyers and Colourists[5] and fastness to washing and chlorine have been determined by the I.C.I. method.[6]

The brazanquinone vat dyes gave purple, blue and bluish black coloured solutions in concentrated sulphuric acid, although majority of them gave blue solutions in common with other brazanquinone derivatives.[7]

TABLE I

Compound	Colour in sulphuric acid	Colour of the vat	Shade on cotton	Fastness		
				Light	Severe washing	Chlorine
(III)	Blue-black	Deep red-brown	Bright orange yellow	5–6	5	5
(IV)	Bright-blue	Red-brown	Bright yellow	3–4	5	5
(V)	Bright-blue	Violet-red	Bright orange yellow	3–4	5	4–5
(VI)	Purple	Deep red	Bright orange yellow	4–5	3–4	4
(VII)	Bright-blue	Violet-red	Pale orange	4–5	3–4	4–5
(VIII)	Blue	Brownish violet	Bright yellow	5	3	4–5
(IX)	Bluish black	Violet-red	Dull yellow	5–6	5	4
(X)	Bluish black	Brownish violet	Orange-yellow	5	3	3
(XI)	Bluish black	Dirty violet	Dull brown-orange	4	5	4
(XII)	Bright-blue	Dark brown-violet	Brownish yellow	4–5	2–3	2–3

The dyes (III), (IV) and (XII) were difficult to reduce, but after precipitation from sulphuric acid they vatted readily. The dyes (VII) to (XI) were dyed by the IN process (50–60°), (III) was dyed at 70–80° and the other dyes were dyed at 60–70°. Higher temperatures employed in the case of the latter dyes are due to the difficulty in vatting at lower temperatures. The shades obtained were yellow, orange-yellow or brownish yellow. The dyes had moderate to good light fastness and had good fastness to severe washing and chlorine. Comparison of the substantivity of the dyes was made on the basis of the depth of the shade and the exhaustion of the dye-baths.

SUMMARY

Brazanquinone vat dyes have been prepared by the condensation of 2: 3-dichloro-1: 4-naphthoquinone (I) with compounds of the Naphtol AS series. Whereas the introduction of halogens and methoxyl groups in the anilide half of Naphtol AS gives more substantive naphthols, derivatives of 1: 2-benzobrazanquinone-4-carboxyanilide (III) which contain these substituents in the carboxyanilide part do not show higher substantivity than (III). The dyes gave yellow, orange-yellow and brownish yellow shades which are moderately fast to light and had good fastness to severe washing and chlorine.

We are indebted to the Council of Scientific and Industrial Research for the award of a Fellowship to one of us (B.S.) and to Dr. T. S. Gore for the microanalyses recorded in the paper.

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5. *J. Soc. Dyers and Col.*, 1940, **56**, 273.
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7. Buu-Hoï .. *J.C.S.*, 1952, 489.

NAPHTHOQUINONE SERIES—PART III

Brazanquinone Vat Dyes from 2: 3-Dichloro-1: 4-Naphthoquinone: Part III

By B. Suryanarayana and B. D. Tilak, F.A.Sc.

(*Department of Chemical Technology, University of Bombay, Bombay* 19)

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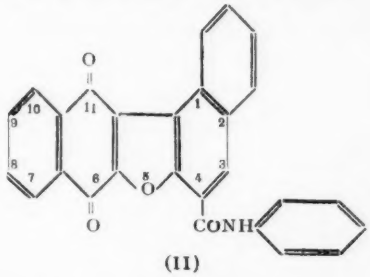
Synthesis of a series of brazanquinone vat dyes by the condensation of 2: 3-dichloro-1 : 4-naphthoquinone (I) with 4-bromo-1-naphthol, 6-bromo-2-naphthol, 2-hydroxy-3-naphthanilide (Naphtol AS) and its derivatives has been described in previous communications.[1, 2] Whereas introduction of halogens, methyl, methoxy and nitro groups in Naphtol AS leads to the more substantive Naphtols, the brazanquinone vat dyes which resulted by the condensation of these Naphtol AS derivatives with (I) did not show superior substantivity or fastness than the parent 1 : 2-benzobrazanquinone-4-carboxyanilide (II) which was obtained from Naphtol AS. Brazanquinone vat dyes described earlier gave yellow, orange-yellow and brownish-

(I)



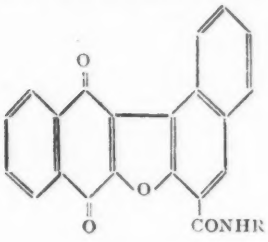
(II)

yellow shades on cotton. With the view to extend the range of shades and also with the view to synthesise dyes of higher substantivity and fastness, (I) was condensed with Naphtols in which the carboxyanilide half of Naphtol AS is replaced by arylides from naphthalene and dibenzofuran and with Naphtols derived from more complex *o*-hydroxycarboxyarylides. These Naphtols are highly substantive and give azoic shades of excellent fastness.

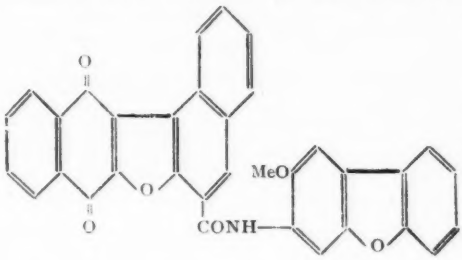
Reaction of (I) with 2-hydroxy-3-naphthoic-α-naphthalide (Naphtol AS-BO) and 2-hydroxy-3-naphthoic-β-naphthalide (Naphtol AS-SW) gave 1 : 2-benzobrazanquinone-4-carboxy-α-naphthalide (III) and 1 : 2-benzobrazanquinone-4-carboxy-β-naphthalide (IV) respectively. The substantivity of these dyes was very good and they gave bright orange yellow shades.

The dye (IV) containing the β-naphthalide group had good fastness to light and chlorine but was poor in washing fastness. The α-naphthalide was not so fast.

Naphtol AS-S [2-hydroxy-3-naphthoic-3′-(2′-methoxydibenzofurano)-amide] is highly substantive on account of the presence of the heterocyclic dibenzofuran ring system. However, 1 : 2-benzobrazanquinone-4-carboxy-3′-(2′-methoxydibenzofurano)-amide (V), a brown dye obtained by the

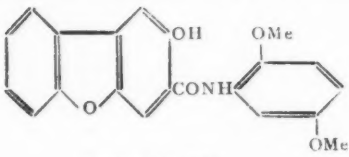


(III) R = α-Naphthyl
(IV) R = β-Naphthyl

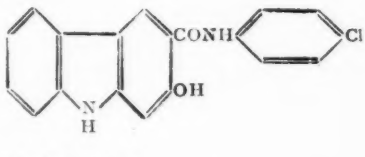


(V)

condensation of Naphtol AS-S with (I), had lower substantivity than (II) and the fastness properties were also poor.



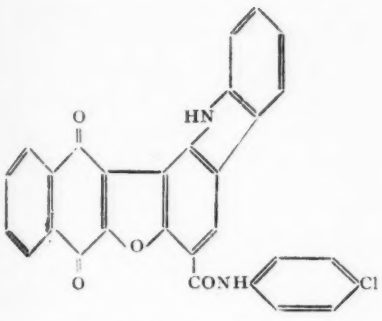
Naphtol AS-BT



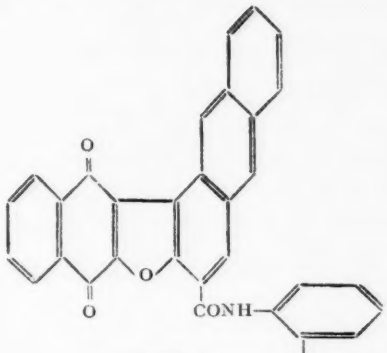
Naphtol AS-LB

Whereas Naphtol AS-BG (2-hydroxy-3-naphthoic-2′ : 5′-dimethoxy-anilide) readily reacts with (I) to give a brazanquinone vat dye,[2] Naphtol AS-BT (2-hydroxydibenzofurano-3-carboxy-2′ : 5′-dimethoxyanilide) does not condense with (I) in pyridine. Attempts to react (I) with 2-hydroxydibenzofuran were also unsuccessful. More complex brazanquinone vat dyes were, however, prepared by the condensation of (I) with compounds of the Naphtol AS series derived from other heterocyclic and higher polycyclic *o*-hydroxycarboxyarylides. Reaction of (I) with 2-hydroxycarbazole-3-carboxy-*p*-chloranilide (Naphtol AS-LB) and 2-hydroxyanthracene-3-carboxy-*o*-toluidide (Naphtol AS-GR) gave 1 : 2-(2′ : 3′-indolo)-brazanquinone-4-carboxy-*p*-chloranilide (VI) and 1 : 2-(2′ : 3′-naphtho)-brazanquinone-4-carboxy-*o*-toluidide (VII) respectively. These compounds were deeply coloured, the former being brick-red and the latter bright violet but they had poor affinity to cotton. The weak shades obtained had however excellent fastness to

light. Whereas Naphtol AS-LB reacted with (I), carbazole did not react under similar conditions.



(VI)



(VII)

In general in contrast to the Naphtol AS series where increase in structural complexity leads to increase in substantivity, brazanquinone vat dyes derived from the more complex Naphtols do not show higher substantivity or fastness and the parent member of the series 1 : 2-benzobrazanquinone-4-carboxyanilide (II) itself has better fastness, substantivity and brightness than these more complex dyes.

The above vat dyes were not readily reduced with alkaline hydrosulphite but after precipitation from sulphuric acid the finely divided dyes were easily vattable. However, the dye (VI) gave a different shade after precipitation from sulphuric acid (dull brownish red → dull brown). The range of shades obtainable from the brazanquinone dyes described in this and the previous papers[1, 2] varies from yellow to violet, although most of them dye bright yellow or orange-yellow shades. The substantivity in most cases is good and the fastness properties of the dyes are also satisfactory.

Experimental

1 : 2-*Benzobrazanquinone*-4-*carboxy*-α-*naphthalide* (*III*)

Naphtol AS-BO (3·1 g.), 2 : 3-dichloro-1 : 4-naphthoquinone (I) (2·2 g.) and pyridine (30 c.c.) were refluxed for 3 hours. The crystalline product (2 g.), m.p. 328–29°, after two recrystallizations from nitrobenzene, gave lustrous red elongated plates, m.p. 328° (Found: N, 3·0. $C_{31}H_{17}NO_4$ requires N, 3·0%).

1 : 2-*Benzobrazanquinone*-4-*carboxy*-β-*naphthalide* (*IV*)

Naphtol AS-SW (3·1 g.), (I) (2·2 g.) and pyridine (30 c.c.) were boiled under reflux for 3 hours and cooled to room temperature. The crystalline

product (2·1 g.), m.p. 292–300°, after recrystallization from pyridine gav lustrous yellow needles, m.p. 292° (Found: N, 3·4. $C_{31}H_{17}NO_4$ requires N, 3·0%).

1 : 2-*Benzobrazanquinone*-4-*carboxy*-3′-(2′-*methoxydibenzofurano*)-*amide* (*V*)

Naphtol AS-S (3·0 g.), (I) (1·8 g.) and pyridine (35 c.c.) were boiled under reflux and the brownish orange crystalline residue (1·6 g.), m.p. 348–49°, was recrystallized from nitrobenzene when it gave elongated brick-red needles, m.p. 348–49° (Found: C, 75·8; H, 3·9; N, 2·7. $C_{34}H_{19}NO_6$ requires C, 75·9; H, 3·5; N, 2·6%).

1 : 2-(2′ : 3′-*indolo*) *brazanquinone*-4-*carboxy*-p-*chloranilide* (*VI*)

Naphtol AS-LB (3·4 g.), (I) (2·2 g.) and pyridine (30 c.c.) were boiled under reflux for 3 hours and the violet-red crystalline product (0·5 g.), m.p. 350–54°, which separated was collected and recrystallized from *o*-dichlorobenzene when it gave brick-red needles, m.p. 354–55° (Found: C, 70·3; H, 3·2; N, 5·8. $C_{29}H_{15}ClN_2O_4$ requires C, 70·9; H, 3·1; N, 5·7%).

1 : 2-(2′ : 3′-*naphtho*) *brazanquinone*-4-*carboxy*-o-*toluidide* (*VII*)

Naphtol AS-GR (1·4 g.), (I) (1·0 g.) and pyridine (15 c.c.) were boiled under reflux. The mixture became viscous owing to separation of a red coloured product. It was, therefore, diluted with pyridine (20 c.c.) and refluxing continued for 3 hours more. The mixture was cooled and filtered. The residue was washed with alcohol and ether, when lustrous violet-red flat needles (1·5 g.), m.p. 345–46°, were obtained. Recrystallization from *o*-dichlorobenzene gave lustrous violet elongated needles, m.p. 346–47° (Found: C, 79·4; H, 3·8; N, 2·6. $C_{32}H_{19}NO_4$ requires C, 79·8; H, 3·9; N, 2·9%).

Colour reactions and dyeing properties

The colour in sulphuric acid, the colour of the vats, the shades on cotton, and the fastness properties of the dyes are given in Table I. Fastness to severe washing and chlorine were determined by the I.C.I. method[4] and fastness to light was determined using the Atlas Fade-O-Meter and following the standards of the Society of Dyers and Colourists.[5]

With the exception of (III) and (VII), which were dyed by the IN process (at 50–60°), the other dyes were dyed at 70–80°. The dyes gave yellow to violet shades which had good fastness to light and chlorine and moderate to good fastness to washing.

TABLE I

Compound	Colour in sulphuric acid	Colour of the vat	Shade on cotton	Fastness		
				Light	Severe washing	Chlorine
(II)	Blue-black	Deep red brown	Bright orange yellow	5–6	5	5
(III)	Blue-black	Brownish violet	Reddish orange	5	3–4	4
(IV)	Blue-black	Brownish violet	Bright orange yellow	6	2–3	4
(V)	Brown	Dirty red	Brownish yellow	4–5	4	4–5
(VI)	Bright greenish blue	Red-brown	Dull brownish red	6–7	3	4–5
(VII)	Olive green	Olive green	Dull violet	6–7	5	3–4

SUMMARY

Naphtols AS-BO, AS-SW, AS-S, AS-LB and AS-GR were condensed with 2: 3-dichloro-1: 4-naphthoquinone (I) with the view to prepare brazanquinone vat dyes of higher substantivity and fastness than 1: 2-benzobrazanquinone-4-carboxyanilide (II). Whereas the above Naphtols are highly substantive, the brazanquinone vat dyes obtained from them were less substantive than (II). The dyes gave yellow to violet shades which had good fastness to light and chlorine and moderate fastness to washing.

We are indebted to the Council of Scientific and Industrial Research for a Fellowship awarded to one of us (B.S.) and to Dr. T. S. Gore for the microanalyses recorded in the paper.

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SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

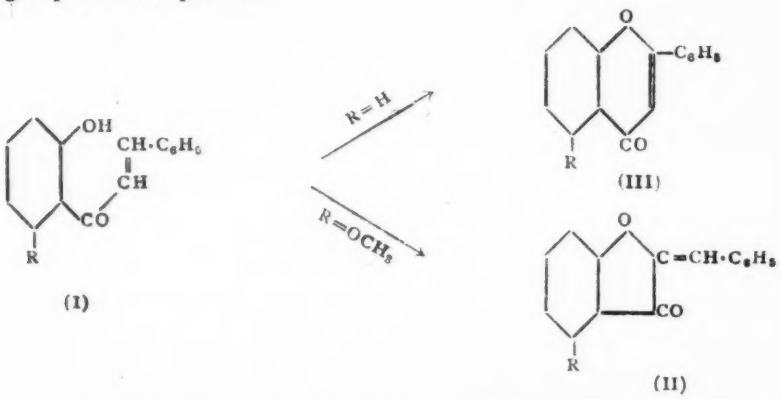
Part XX. Hydrogen Peroxide Oxidation of Some α-Methoxy Chalkones and Synthesis of Some Partial Methyl Ethers of Quercetin

By N. Narasimhachari, S. Narayanaswami and T. R. Seshadri, F.A.Sc.

(From the Department of Chemistry, Delhi University)

Received October 14, 1952

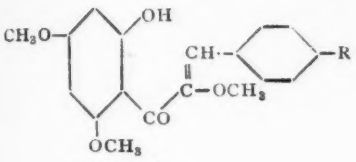
Chalkones constitute important intermediates in the synthesis of flavanones, flavones and flavonols. The method originally adopted by Kostanecki[1] for obtaining flavonols from chalkones through the flavanones and their isonitroso derivatives has been largely replaced by the direct method employing alkaline hydrogen peroxide. This reaction discovered by Algar and Flynn[2] is influenced considerably by the presence of substituents particularly in the 6-position of the chalkone (I) and benzalcoumaranones (II) are formed in many cases instead of flavonols (III).[3, 4] However this difficulty has been reported[5] to be counteracted by the presence of a hydroxyl group in the 4′-position.



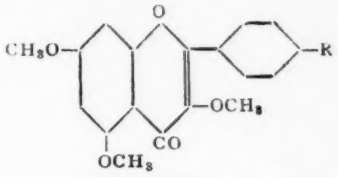
The dual course of this reaction mentioned above can give rise to ambiguity in the nature of the product unless adequate precautions are taken. The formation of mixtures cannot be ruled out. It was expected that the presence of a methoxyl in the α-position of the chalkone would eliminate this difficulty and yield only flavonol derivatives even when the 6-position is substituted, since on any of the mechanisms advocated in the past,[3, 5] the

presence of a free hydrogen atom in this position is necessary for the formation of benzalcoumaranones. Such α-methoxy chalkones have now been obtained in good yields. They undergo smooth oxidation with alkaline hydrogen peroxide to yield the corresponding flavonol methyl ethers. Besides removing the ambiguity in the nature of the product this procedure provides a good preparative method.

ω-Methoxy phloracetophenone dimethyl ether is condensed with benzaldehyde and anisaldehyde to yield 2-hydroxy-α: 4: 6-trimethoxy and 2-hydroxy-α: 4: 6: 4′-tetramethoxy chalkones (IV and V).[6] On treating these chalkones with alkaline hydrogen peroxide good yields of galangin trimethyl ether (VI) and kæmpferol tetramethyl ether (VII) identical with authentic samples are obtained. One of the main advantages of this method is the absence of a free hydroxyl group in the 3-position of the product, thus adding greatly to its stability to further oxidation by alkaline hydrogen peroxide and producing good yields.



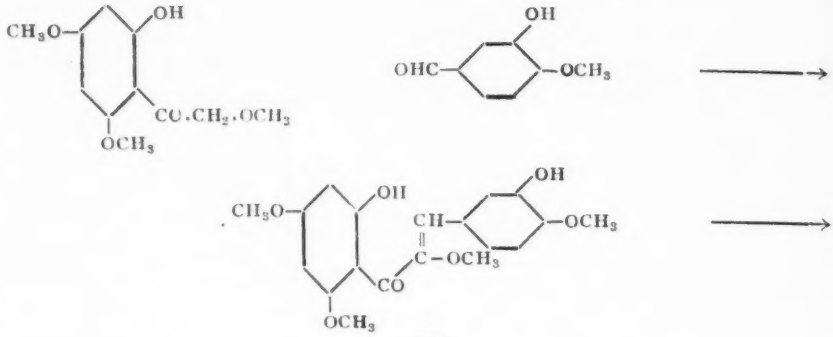
(IV) R=H
(V) R=OCH_3



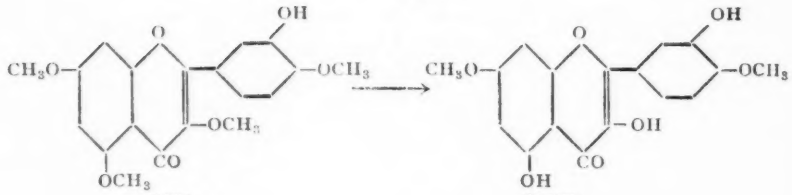
(VI) R=H
(VII) OCH_3

The abovementioned method could be employed in conjunction with partial demethylation for the preparation of partial methyl ethers of flavonols many of which are important naturally occurring compounds. As typical examples the syntheses of 7: 4′-dimethyl ether of quercetin (now named isorhamnazin, VIII) and 3: 5: 7-trimethyl ether of quercetin (IX) have now been carried out. 2-Hydroxy-ω: 4: 6-trimethoxy acetophenone is condensed with isovanillin in the presence of alcoholic potassium hydroxide. The resulting 2: 3′-dihydroxy-α: 4: 6: 4′-tetramethoxy chalkone (X) is oxidised with alkaline hydrogen peroxide at 0°. The product obtained on acidification is almost colourless, gives no colour with ferric chloride, but produces a red colour with magnesium and hydrochloric acid thus agreeing with the requirements of a flavonol structure. It resembles in all its properties 3′-hydroxy-5: 7: 3: 4′-tetramethoxy flavone (XI) recently reported by King, *et al.*,[7] in the course of their work on the synthesis of ayanin. They adopted the Allan-Robinson condensation using ω-methoxy phloracetophenone and the anhydride and sodium salt of benzyl isovanillic acid, methylated the product and finally removed the benzyl group. The present

method is simpler to carry out and consists of less number of stages giving better yields.



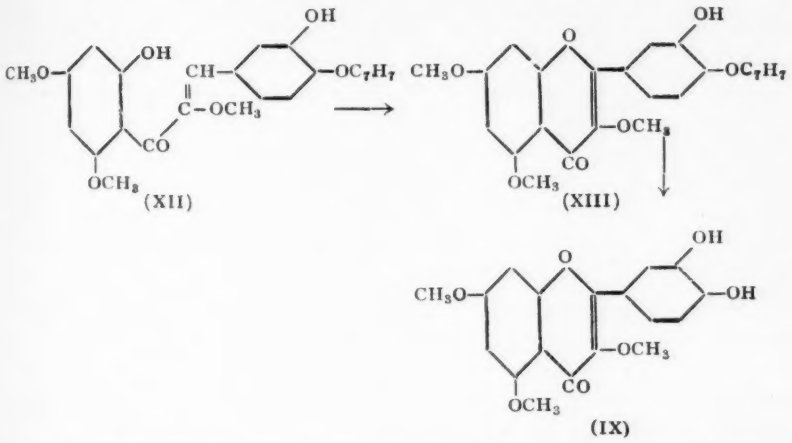
(X)



(XI) (VIII)

The tetramethoxy monohydroxy flavonol (XI) yields on methylation the well-known pentamethyl quercetin. The tetramethyl ether (XI) has been subjected to partial demethylation with anhydrous aluminium chloride in nitrobenzene solution. This method is known to bring about demethylation in the 3- and 5-positions. The product is a dimethyl ether giving greenish yellow fluorescence in conc. sulphuric acid and a deep olive brown colour with ferric chloride in alcohol. Its m.p. is 201–03°. Based on these properties and on the established course of the reaction it is given the constitution of 7: 4′-O-dimethyl quercetin (VIII) and the trivial name of isorhamnazin since it could also be expected to occur in nature.

ω-Methoxy phloracetophenone dimethyl ether is condensed with the 4′-benzyl ether of protocatechuic aldehyde and the resulting 2: 3′-dihydroxy-4′-benzyloxy-α: 4: 6-trimethoxy chalkone (XII) oxidised with alkaline hydrogen peroxide. The product gives all the reactions of a flavonol derivative (XIII). When debenzylated with conc. hydrochloric acid in acetic acid solution the 3: 5: 7-trimethyl ether of quercetin (IX) is obtained. This partial methyl ether of quercetin has not so far been reported in the literature and should serve as a useful intermediate for the preparation of rhamnetin.



The flavonol methyl ethers could also be obtained from α-methoxy chalkones by direct dehydrogenation with selenium dioxide. In this case the course of the reaction is obvious. It should first undergo change to the corresponding 3-methoxy flavanone under the conditions of heating and then suffer dehydrogenation. A similar mechanism could be suggested for the oxidation with alkaline hydrogen peroxide also. It is not unusual for flavanones to be produced to some extent in alkaline media. Actually in many condensations using alkali the chalkones are produced along with the corresponding flavanones.[8] The removal of the flavanone by dehydrogenation with hydrogen peroxide may be expected to accelerate the production of more flavanone from the chalkone leading to the eventual production of flavonol methyl ether in good yield.

The simplest of the *o*-hydroxy chalkones containing a substituent in the 6-position is 2-hydroxy-6-methoxy chalkone. Oliverio and Schiavello[9] claimed to have obtained 5-methoxy flavonol by oxidising it with hydrogen peroxide. Repetition of this oxidation in this laboratory has yielded only 4-methoxy benzalcoumaranone as the sole product. In view of this and other contradictory results the Algar-Flynn reaction seems to require more detailed investigation.

Experimental

Oxidation of 2-hydroxy-α: 4: 6-trimethoxy chalkone to galangin trimethyl ether:

(i) *With hydrogen peroxide.*—2-Hydroxy-α: 4: 6-trimethoxy chalkone[6] (1 g.) was dissolved in a mixture of aqueous sodium hydroxide (6·4 c.c.,

1 N.) and pyridine (5 c.c.) and the solution cooled well with crushed ice. Aqueous hydrogen peroxide (5·5 c.c., 5%) was added to it dropwise and the solution left in the refrigerator overnight. A colourless product separated and more was obtained on diluting the solution with water (60 c.c.). It was filtered and washed with water. It crystallised from alcohol as colourless needles melting at 195–97°. The mixed melting point with an authentic sample of galangin trimethyl ether[10] was not depressed. Yield 0·65 g. The alkaline filtrate on acidification gave a little of the original chalkone (m.p. and mixed m.p. 118°).

(ii) *With selenium dioxide.*—The chalkone (1 g.) was mixed with dry selenium dioxide (1 g.) and the mixture heated under reflux with amyl alcohol (20 c.c.) at 140° for 12 hours. After cooling it was filtered and the black selenium on the filter washed with hot rectified spirits. Amyl alcohol was removed by distillation under reduced pressure, the last traces being removed by passing in a current of steam. The residue was twice crystallised from alcohol when it was obtained as colourless needles melting at 195–97°; a mixed melting point with the sample obtained in experiment (i) was undepressed. Yield 0·4 g.

Oxidation of 2-*hydroxy*-α : 4 : 6 : 4′-*tetramethoxy chalkone to kæmpferol tetramethyl ether*

(i) *With hydrogen peroxide.*—To a cooled solution of 2-hydroxy-α : 4 : 6 : 4′-tetramethoxy chalkone (0·5 g.) in aqueous sodium hydroxide (0·12 g. in 3 c.c. of water) hydrogen peroxide (2 c.c. of 5%) was added slowly when a solid separated. Pyridine (2 c.c.) was added to get a clear solution which was left in the refrigerator overnight. The product, on working up as in the previous experiment, crystallised from alcohol as colourless needles melting at 165–66°. It was identical with kæmpferol tetramethyl ether[11] (mixed m.p. 165–66°). Yield 0·3 g.

(ii) *With selenium dioxide.*—The chalkone (0·42 g.) was mixed with selenium dioxide (0·42 g.) and amyl alcohol (20 c.c.). After refluxing for 12 hours it was treated in exactly the same manner as described in the earlier case. The product on crystallising twice from alcohol melted at 165–66° and the mixed melting point with the above sample of kæmpferol tetramethyl ether was undepressed. Yield 0·2 g.

2 : 3′-*Dihydroxy*-α : 4 : 6 : 4′-*tetramethoxy chalkone* (*X*)

ω-Methoxy phloracetophenone dimethyl ether (1 g.) and *iso*-vanillin (0·7 g.) were dissolved in alcohol (10 c.c.) and the solution treated with a strong solution of potassium hydroxide (2·5 g. in 2·5 c.c. of water). More

alcohol (25 c.c.) was added and the solution kept for 24 hours. A bright yellow solid separated which was brought into solution by heating and the solution refluxed on a water-bath for one hour and again left at room temperature overnight. On diluting with water a white turbidity appeared which cleared on extracting with ether. The clear aqueous solution when acidified gave a sticky mass which turned a definite solid on being kept in the refrigerator. It was filtered, washed with saturated sodium bicarbonate solution and finally with water. Crystallisation once from alcohol and again from ethyl acetate yielded the chalkone as golden yellow prisms and prismatic needles melting at 193–94°. It gave a brown colour with ferric chloride in alcoholic solution. Yield 0·8 g. (Found: C, 63·0; H, 5·6; $C_{19}H_{20}O_7$ requires C, 63·3; H, 5·6%).

3:5:7:4′-*Tetramethoxy*-3′-*hydroxy flavone* (*XI*)

The above chalkone (1 g.) was dissolved in aqueous sodium hydroxide (4 g. in 20 c.c. of water) and the solution diluted with water (50 c.c.). It was cooled well in ice and aqueous hydrogen peroxide (5 c.c. of 16%) was added to it slowly and left in the refrigerator for 12 hours. A pale yellow solid (A) separated which was filtered and the filtrate acidified with hydrochloric acid when a crystalline solid was obtained; this was collected, washed with aqueous bicarbonate (in which it was insoluble) and water. It crystallised from alcohol as lens-shaped and rhombic plates melting at 223–24°. The original solid (A) that separated from the alkaline solution also melted at 223–24° on crystallisation and the two fractions were identical. Recrystallisation from glacial acetic acid did not alter the melting point. It gave no colour with ferric chloride and with magnesium and hydrochloric acid its alcoholic solution developed a magenta colour. It agreed closely in its properties and reactions with 3:5:7:4′-tetramethoxy-3′-hydroxy flavone described by King, *et al.*, who reported the m.p. as 220–22° (Found: C, 58·3; H, 5·5; $C_{19}H_{18}O_7$, $2H_2O$ requires C, 57·9; H, 5·6%).

The acetate crystallised from alcohol as aggregates of small rectangular prisms melting at 147–48° (Found: C, 62·5; H, 5·0; $C_{21}H_{20}O_8$ requires C, 63·0; H, 5·0%).

On refluxing the above 3′-hydroxy compound with dimethyl sulphate and anhydrous potassium carbonate in acetone solution and crystallising the product from dilute alcohol quercetin pentamethyl ether was obtained; m.p. and mixed m.p. 143–44°.

7:4′-*Dimethoxy*-3:5:3′-*trihydroxy flavone* (*Isorhamnazin*) (*VIII*)

The above tetramethyl ether of quercetin (XI) (0·6 g.) was mixed with anhydrous aluminium chloride (2 g.) and dry nitrobenzene (10 c.c.) and the

mixture refluxed over a water-bath for 2 hours. After allowing it to cool, petroleum ether was added to precipitate the complex. The supernatant liquid was decanted and the residue washed with petroleum ether repeatedly to remove nitrobenzene. The aluminium chloride complex was treated with ice and hydrochloric acid (20 c.c.). The last traces of nitrobenzene were removed by passing in steam. The pale brown solid that separated was filtered and washed with water. The product was acetylated after drying by refluxing with acetic anhydride and pyridine at 140° for 2 hours. On pouring the mixture into crushed ice a pale brown solid was obtained. After a crystallisation from alcohol the product was still coloured. It was therefore taken in boiling ethyl acetate, treated with animal charcoal and filtered. The clear filtrate was treated with petroleum ether till there was turbidity which on allowing to stand cleared up depositing a sticky mass. The clear solution was decanted off, treated with more petrol and warmed to get a clear solution. On cooling it colourless stout prisms separated out; m.p. 198–200° (Found: C, 60·4; H, 4·5; $C_{23}H_{20}O_{10}$ requires C, 60·5; H, 4·4%).

The above acetate was dissolved in boiling alcohol (2 c.c.) and refluxed for 15 minutes with conc. hydrochloric acid (2 c.c.). A pale brown powder separated on cooling which crystallised from alcohol as yellow aggregates of small prisms melting at 201–03° (Found: in air-dried sample: C, 58·6; H, 4·6; loss on drying 2·5; $C_{17}H_{14}O_7$, H_2O requires C, 58·6; H, 4·6; loss of $\frac{1}{2}$ H_2O 2·6%. Found in a sample dried *in vacuo* at 140° for 2 hours: C, 59·8; H, 4·5; $C_{17}H_{14}O_7$, $\frac{1}{2}$ H_2O requires C, 60·1; H, 4·4%). The product gave an olive brown colour with ferric chloride in alcohol; with concentrated sulphuric acid it gave a solution exhibiting greenish yellow fluorescence and with aqueous alkali a bright yellow solution.

4-Benzyl protocatechuic aldehyde

The preparation of this is reported only in patent literature.[12] It is formed along with the 3-benzyl compound by heating protocatechuic aldehyde with benzyl chloride in alcoholic potassium hydroxide. It has now been prepared by two methods; the easier method uses benzyl chloride and anhydrous potassium carbonate in dry acetone medium.

(i) Protocatechuic aldehyde (4 g.) and benzyl chloride (3·5 c.c., 1 mole) were refluxed in acetone solution (150 c.c.) with anhydrous potassium carbonate (15 g.) for 20 hours. The potassium salts were filtered, washed with hot acetone and acetone distilled off from the filtrate. Steam was passed through the residue to remove the last traces of unreacted benzyl chloride; after cooling the mixture water was decanted off leaving a semisolid mass. On adding a little alcohol and scratching, the whole mass solidified and was

separated into alkali-soluble and alkali-insoluble fractions as follows. The product was first treated with aqueous sodium carbonate (5%) in which it was found to be completely insoluble. On treatment with sodium hydroxide most of it went into the solution leaving a little residue which was separated by filtration. Acidification of the alkaline solution gave a colourless solid which crystallised from alcohol as colourless rectangular rods melting at 121–22° (reported[12] m.p. of the 4-benzyl ether 122°); yield 3·2 g. The alkali-insoluble residue (dibenzyl ether, not reported earlier) crystallised from alcohol as stout rectangular prisms and rods melting at 93–94° (Found: C, 78·7; H, 5·7; $C_{21}H_{18}O_3$ requires C, 79·2; H, 5·7%).

(ii) Protocatechuic aldehyde (4 g.) and benzyl chloride (4·25 c.c.) were refluxed in alcoholic solution (60 c.c.) with sodium bicarbonate (10 g.) for 10 hours. The mixture was then filtered and alcohol was distilled off from the filtrate. The oily residue was well digested with sodium carbonate in which the 3-benzyl ether was soluble (solution A). The carbonate-insoluble residue was next treated with sodium hydroxide (5%) solution which dissolved the 4-benzyl ether (solution B) and the final residue (C) consisted of the dibenzyl ether.

The product obtained on acidifying the carbonate solution (A) crystallised from alcohol as colourless needles melting at 113–14° (reported m.p. for the 3-benzyl ether 113°)[12]; yield 0·5 g. The sodium hydroxide solution (B) on acidification gave the 4-benzyl ether (m.p. 121–22° from alcohol); yield 2·1 g. The dibenzyl ether (alkali-insoluble residue C) crystallised from alcohol as colourless stout rectangular prisms melting at 93–94° (identical with the sample described in experiment (i). Yield 1·8 g.

2: 3′-*Dihydroxy*-α : 4: 6-*trimethoxy*-4′-*benzyloxy chalkone* (*XII*)

ω-Methoxy phloracetophenone dimethyl ether (0·6 g.) and 4-benzyl protocatechuic aldehyde (0·6 g.) were dissolved in alcohol (20 c.c.) by warming and a solution of potassium hydroxide (1·8 g. in 2 c.c. of water) was added. The solution was refluxed for two hours when all the solid dissolved and a deep red solution was obtained. It was kept corked for 48 hours; the solution was diluted when some turbidity appeared which was cleared by ether extraction. On acidification and cooling in ice an oily product was obtained. The aqueous layer was decanted, the oily product taken in ether and washed with aqueous sodium bicarbonate solution. Attempts to crystallise the chalkone were not successful and hence it was directly used for oxidation.

3′-Hydroxy-3 : 5 : 7-trimethoxy-4′-benzyloxy flavone (XIII)

The above chalkone (1 g.) was dissolved in a mixture of sodium hydroxide (5 g. in 60 c.c. of water) and pyridine (5 c.c.). The clear solution was cooled and hydrogen peroxide (6 c.c., 16%) was added slowly. After the addition was complete the solution was left in the refrigerator for 12 hours. A pale yellow solid separated which was filtered and washed with water. It crystallised from alcohol as colourless tiny prisms melting at 201–03°. Acidification of the alkaline solution and crystallisation gave the same product (m.p. and mixed m.p. 201–03°. It gave no colour with ferric chloride but gave a red colour with magnesium and hydrochloric acid in alcoholic solution (Found: C, 68·8; H, 4·8; $C_{25}H_{22}O_7$ requires C, 69·1; H, 5·1%).

3 : 5 : 7-Trimethoxy-3′ : 4′-dihydroxy flavone (IX)

The above 4′-benzyloxy flavonol (0·2 g.) was dissolved in minimum quantity of glacial acetic acid (4 c.c.) and the solution heated with conc. hydrochloric acid (4 c.c.) for 30 minutes on a water-bath. It was then cooled, diluted with water and the acids neutralised by adding carefully solid sodium bicarbonate. The solid which separated was crystallised from alcohol when it was obtained as tiny prisms melting at 282–84° (decomp.). It gave a green colour with ferric chloride in alcoholic solution and magenta colour with magnesium and hydrochloric acid (Found: C, 63·1; H, 5·1; $C_{18}H_{16}O_7$ requires C, 62·8; H, 4·7%).

Oxidation of 2-hydroxy-6-methoxy chalkone

The chalkone (2 g.) was dissolved in a solution of sodium hydroxide (4 g. in 70 c.c. of water) and treated with aqueous hydrogen peroxide (5 c.c., 16%) under the usual conditions. A bright yellow solid slowly separated. After leaving overnight it was filtered, washed with water and crystallised from excess of alcohol. It melted at 189–90° and further crystallisations did not raise the melting point. It gave a red colour with conc. sulphuric acid, no colour with alcoholic ferric chloride and was insoluble in aqueous alkali (Found: C, 70·7; H, 5·0; $C_{16}H_{12}O_3$, H_2O requires C, 71·1; H, 5·2%). Thus it possessed the properties expected of 4-methoxy benzalcoumaranone. The alkali filtrate on acidification and extraction with ether gave no product. Yield 0·8 g.

SUMMARY

A new method of synthesis of flavonols is described. It involves the oxidation of α-methoxy chalkones with alkaline hydrogen peroxide. The special advantages are (1) it avoids the formation of benzal coumaranones and (2) it gives good yields owing to the stability to further oxidation

conferred by the 3-methoxyl group. The same products are obtained using selenium dioxide as the oxidising agent. Complete methyl ethers of galangin and kæmpferol have been prepared. The method is also useful for the preparation of partial methyl ethers of flavonols. 3:5:7:4′-Tetramethyl ether of quercetin and 3:5:7-trimethyl ether of quercetin are prepared. The former has been subjected to partial demethylation to yield the new 7:4′-dimethyl ether of quercetin which is now named isorhamnazin.

Under ordinary conditions 2-hydroxy-6-methoxy chalkone yields with alkaline hydrogen-peroxide only 4-methoxy benzalcoumaranone and not 5-methoxy flavonol as claimed by Oliverio and Schiavello.

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SULPHUR ISOSTERS OF CARCINOGENIC HYDROCARBONS

Part II. 6: 12–Dimethylbenzo(1: 2-*b*, 5: 4-*b'*)dithionaphthene and Thionaphtheno(4: 5: 4′: 5′)thionaphthene

By V. V. Ghaisas, K. Rabindran and B. D. Tilak, F.A.Sc

(*Department of Chemical Technology, University of Bombay*)

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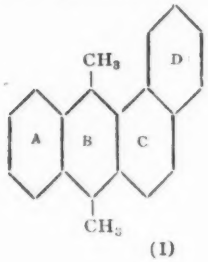
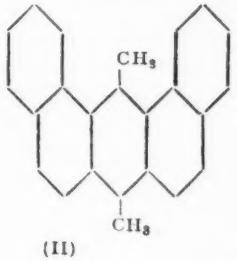
The carcinogenic activity of polycyclic hydrocarbons has been related by Robinson[1] to the presence of an "activated phenanthrene bridge". With a view to study the significance of the phenanthrene bridge in chemical carcinogenesis, sulphur isosters of carcinogenic hydrocarbons in which an appropriate benzene ring is replaced by the isosteric thiophene nucleus were synthesized. The synthesis of 4: 9-dimethyl-2: 3-benzothiophanthrene (III) and 4: 9-dimethyl 2: 3: 5: 6-dibenzothiophanthrene (IV) which are sulphur isosters of 9: 10-dimethyl-1: 2-benzanthracene (I) and 9: 10-dimethyl-1: 2: 7: 8-dibenzanthracene (II), has been described in the previous communication.[2] Compound (III), where the phenanthrene bridge in (I) is removed by isosteric replacement of the benzene ring C, is inactive by subcutaneous injection in mice and weakly active on painting. It is highly



(I)



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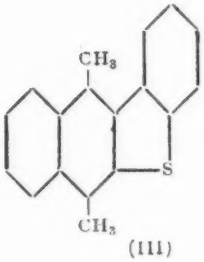

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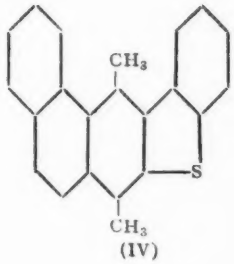
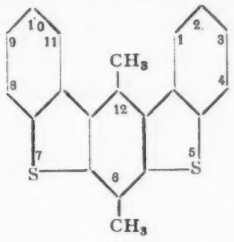


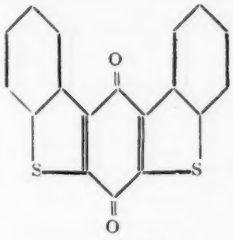
(IV)

significant that high activity again emerges in the benzo derivative (IV) where the phenanthrene double bond is once again introduced.

The present paper records the synthesis of the important key compound, 6: 12-dimethylbenzo(1 : 2-*b*, 5 : 4-*b'*)dithionaphthene (V) which is the sulphur isoster of (II) where both the phenanthrene double bonds have been removed and the *meso*-positions blocked by methyl groups. The name and numbering of (V) follows from the corresponding benzodithiophene.[3] If (V) proves



(V)

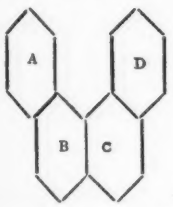


(VI)

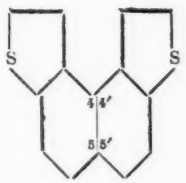
to be non-carcinogenic, the phenanthrene bridge hypothesis of Robinson will receive strong support.

The benzothionaphthene (V) was prepared from benzo (1 : 2-*b*, 5 : 4-*b'*) dithionaphthene-6 : 12-quinone (VI) through the iodomethyl derivative according to Fieser and Hershberg.[4] The quinone (VI) was prepared according to Mayer[5] starting from thioisatin and *sym*-dichloroacetone.

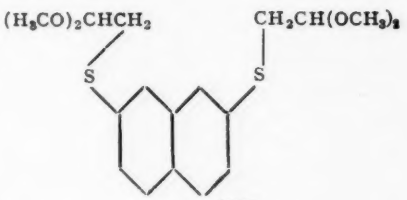
Synthesis of thiophene analogues of carcinogenic polycyclic hydrocarbons related to 1 : 2-benzanthracene have been described above and in the previous paper.[2] The study of carcinogenic activity of another important carcinogen, 3 : 4-benzphenanthrene (VII) has also been undertaken. Isosteric replacement of rings A and D in (VII) should not affect its carcinogenic activity whereas replacement of rings B and C should have profound effect. The synthesis of thionaphtheno(4 : 5, 4' : 5')thionaphthene (VIII), the thiophene analogue of (VII) obtained by replacement of rings A and D, is now described.



(VII)



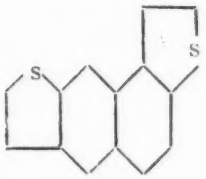
(VIII)



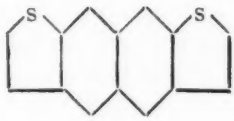
(IX)

2: 7-Naphthalenedithiol was prepared in 76% yield by the reduction of 2: 7-naphthalenedisulphonyl chloride by passing hydrogen chloride into a solution of the disulphonyl chloride and stannous chloride in absolute ethanol saturated with dry hydrogen chloride. It has been prepared previously by the reduction of the disulphonyl chloride with zinc and dilute sulphuric acid[6] (poor yields) or by reduction with zinc and acetic acid[7] (5% yield). 1: 5-Naphthalenedithiol and 2: 6-naphthalenedithiol have likewise been prepared in improved yields by the reduction of the corresponding disulphonyl chlorides with stannous chloride and ethanolic hydrogen chloride.[8] This method of reduction of disulphonyl chlorides to dithiols therefore appears to be more convenient than other methods of reduction.

Condensation of 2: 7-naphthalenedithiol with two molecules of bromoacetaldehyde dimethyl acetal gave 2: 7-*bis*-dimethoxyethylmercapto-naphthalene (IX). Ring-closure of (IX) was effected by treatment with phosphoric acid and phosphorus pentoxide. The cyclization product may be constituted as (VIII), (X) or (XI) depending on the direction of ring-closure of the thioglycolic-aldehyde dimethyl acetal side chains. Compounds (VIII), (X) and (XI) are dithiophene analogues of 3: 4-benzphenanthrene, 1: 2-benzanthracene and naphthacene respectively. Whereas naphthacene is coloured, the cyclization product from (IX) is colourless. In view of the favoured α-cyclization in the naphthalene series, the cyclization product is likely to be constituted as (VIII) rather than (X) or (XI). Further confirmation of this view was derived by comparison of the absorption spectra of the cyclization product with the spectra of 3: 4-benzphenanthrene, 1: 2-benzan-



(X)



(XI)

thracene and naphthacene.[9] The absorption spectrum of the cyclization product is widely divergent from naphthacene. It however shows greater resemblance to 3: 4-benzphenanthrene as compared with 1: 2-benzanthracene. The cyclization product from (IX) is therefore constituted as thionaphtheno-(4: 5: 4′: 5′-) thionaphthene (VIII).

The carcinogenic activity of (V) and (VIII) will be examined in due course.

Experimental

6: 12-*Dimethylbenzo* (1 : 2-*b*, 5 : 4-*b'*) *dithionaphthene* (*V*)

A paste of the quinone (VI) (1·3 g.) in dry thiophene-free benzene (50 c.c.) was added to the Grignard reagent from magnesium (1·3 g.) and methyl iodide (5 c.c.) in dry ether (28 c.c.). It immediately dissolved giving a greenish yellow solution which was boiled under reflux for one hour. After the reaction was over, the mixture was cooled in ice and added gradually to a solution of hydriodic acid, sp. gr. 1·7 (16·8 c.c.) in methyl alcohol (27·4 c.c.) which was cooled in a freezing mixture. A yellow precipitate of the iodomethyl compound separated. The mixture was then diluted with glacial acetic acid (27 c.c.) and the precipitate was collected and dissolved in dioxan (60 c.c.). A mixture of stannous chloride (7·5 g.), concentrated hydrochloric acid (22 c.c.) and dioxan (40 c.c.) was added quickly and the mixture boiled gently for 15 minutes. Dioxan was removed under reduced pressure till the volume was about 30 c.c. The solution was cooled when a yellow product separated (0·382 g.), m.p. 184–88°, which after two crystallizations from benzene-alcohol gave yellow needles of the dithionaphthene (V), m.p. 189–90·5° (Found: C, 75·3; H, 4·5. $C_{20}H_{14}S_2$ requires C, 75·5; H, 4·4%). *sym*-Trinitrobenzene (35 mg.) and pure (V) (50 mg.) were boiled together in dry pure benzene. Concentration and cooling of the solution gave the *sym-trinitrobenzene derivative* as red needles, m.p. 190–1° (Found: C, 58·7; H, 3·0; N, 8·3. $C_{26}H_{17}N_3O_6S_2$ requires C, 58·7; H, 3·2; N, 7·9%).

2: 7-*Naphthalenedithiol*

A mixture of dry sodium 2: 7-naphthalenedisulphonate (20 g.) and phosphorus pentachloride (80 g.) was heated in an oil-bath at 140–50° for 4 hours. Phosphorus oxychloride was removed under reduced pressure and the residue was added to crushed ice. The crude disulphonyl chloride (19 g.) was crystallized from benzene in colourless plates (7·7 g.), m.p. 157°.

The disulphonyl chloride was converted to the dithiol by a modification of the method of Albenga and Corbellini[10] employed for the preparation of 1: 5-naphthalenedithiol. Absolute alcohol (80 c.c.) was saturated with dry hydrogen chloride at room temperature in a three-necked flask fitted with a reflux condenser and a calcium chloride tube. Hydrated stannous chloride (40 g.) was added and the solution heated to boil. A suspension of the disulphonyl chloride (7·7 g.) in dry benzene (60 c.c.) was added in small portions. After each addition a vigorous reaction took place. Dry hydrogen chloride was passed throughout the experiment. The mixture was

refluxed further for 30 minutes and then distilled till 72 c.c. of the solvent distilled over. The residue gave lustrous plates of 2:7-naphthalenedithiol on cooling. The dithiol was collected in a sinter glass crucible and washed repeatedly with concentrated hydrochloric acid (total 50 c.c.) then with water and finally dried in vacuum over phosphorus pentoxide. The thiol (3·8 g., yield 76%) gave m.p. 179° (literature, 174°[6] and 181°[4]).

2:7-*bis*-*Dimethoxyethylmercaptonaphthalene* (*IX*)

2:7-Naphthalenedithiol (17 g.), sodium (5·1 g.), bromoacetaldehyde dimethyl acetal (40·7 g.), and absolute alcohol (200 c.c.) were refluxed on a water-bath for 3 hours. The acetal was isolated by means of ether when it gave a dark oil (25 g.; yield 77%). On crystallization from *n*-hexane, it gave pale yellow needles, m.p. 38° (Found: C, 58·6; H, 6·5. $C_{18}H_{24}O_4S_2$ requires C, 58·7; H, 6·5%).

Thionaphtheno (4:5:4′:5′) *thionaphthene* (*VIII*)

Phosphoric acid, sp. gr. 1·75 (15 c.c.) was added to a mixture of the acetal (IX) (3·0 g.) and phosphorus pentoxide (24 g.) and the mixture was immediately heated in an oil-bath kept at 150–60° for 5 minutes and then diluted into crushed ice. The product was collected and extracted with hot benzene. The benzene extract was washed with aqueous sodium hydroxide, dried and the solvent removed. The yellow crystalline residue (1·29 g.) was redissolved in benzene and the solution passed through activated alumina. The product gave a uniform chromatogram and showed blue fluorescence in ultraviolet light. The chromatographed product was further purified through the picrate. Decomposition of the picrate with 1% ammonia gave a pale yellow product (0·55 g., yield 29%), m.p. 162–63°. After sublimation at 180–200°/10 mm. and crystallization from *n*-hexane, the thionaphthenothionaphthene gave colourless plates, m.p. 163° (Found: C, 69·8; H, 3·5. $C_{14}H_8S_2$ requires C, 70·0; H, 3·3%). The *picrate* gave orange needles from alcohol, m.p. 185° (Found: N, 9·1. $C_{20}H_{11}N_3O_7S_2$ requires N, 9·0%).

SUMMARY

With the view to study the significance of the 9:10-phenanthrene double bond (" phenanthrene bridge ") in 9:10-dimethyl-1:2:7:8-dibenzanthracene (II), 6:12-dimethylbenzo(1:2-*b*, 5:4-*b*′)dithionaphthene (V) was prepared where both the phenanthrene bridges in (II) are removed by isosteric replacement with thiophene rings and the *meso*-positions are blocked by methyl groups. Compound (V) should prove noncarcinogenic.

2:7-Dimethoxyethylmercaptonaphthalene (IX) on cyclization gave thionaphtheno(4:5:4′:5′-)thionaphthene (VIII). The constitution (VIII)

follows from the favoured α-cyclization in the naphthalene series and the similarity of its absorption spectrum with that of 3:4-benzphenanthrene.

We are indebted to the Council of Scientific and Industrial Research or the award of a Fellowship to one of us (K. R.), to Dr. M. R. Padhye and Mr. S. R. Desai for determination of the absorption spectra and to Dr. T. S. Gore for the microanalyses recorded in this paper.

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RATIO OF κ- TO π-MESONS ON FERMI'S THEORY

By D. S. Narayan

(Tata Institute of Fundamental Research)

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1. Introduction

Subsequent to the publication of Fermi's theory on high energy nuclear events (1950, 1951), there is increasing evidence for the existence of heavier types of particles like the κ-meson, V-particles, etc. According to the experiments of the Bristol group (1951), the ratio of κ-mesons to π-mesons is equal to $0{\cdot}6 \pm 0{\cdot}2$ in showers initiated by primaries of energy $>$ 50 B. eV. The fact that appreciable numbers of κ-mesons are emitted indicates that the κ-meson is strongly coupled to the nucleon like the π-meson. This situation is favourable for applying Fermi's method to the calculation of the ratio of κ-mesons to π-mesons. We calculate this ratio under two alternative assumptions namely that either the κ-meson has a spin 0 and a statistical weight 3 or it has a spin $\frac{1}{2}$ and a statistical weight 8. At very high energies the ratio of κ- to π-mesons will be proportional (apart from a slight difference) to their statistical weights. But greater interest attaches to this ratio at moderate energies and the manner in which the number of κ-mesons builds up with the primary energy.

We adopt, in the following, Fermi's approach of statistical thermodynamics. Since in the energy region we are interested in, the κ-meson energies are no longer extremely relativistic, we have to use the exact relation between energy and momentum in the expressions in Fermi s theory.

2. Calculations

We assume that the κ-mesons and the π-mesons are produced in the same volume which is a sphere of radius $R = \frac{\hbar}{m_\pi c} = 1{\cdot}4 \times 10^{13}$, Lorentz contracted to a volume $V = 2\frac{Mc^2}{W} \frac{4}{3} \pi R^3$, where W is the total energy of the colliding nucleons in the centre of mass-system. The average number of particles liberated in V in a state of energy ω and angular momentum z is proportional to

$$1\Big/\left[\exp.\left(\frac{\omega}{\kappa\tau}-\lambda z\right)\pm 1\right],$$

where the + sign is to be taken for Fermi-Dirac statistics and the − sign for Bose-Einstein statistics. The parameters $1/\kappa\tau$ and λ are determined by the conservation of energy and angular momentum. For ω and z we write

$$\omega = c\,(p^2+m^2c^2)^{\frac{1}{2}};\quad z = xp\eta,$$

where $\eta = \cos\theta$, θ being the angle between the direction of motion of the emitted particle and the initial direction of motion of the colliding nucleons. The number of π-mesons liberated in a volume element of the phase space is

$$dN_\pi = \frac{Mc^2 b_-}{2\pi\hbar^3 W}\,\frac{(R^2-x^2)\,dx\,p^2\,dp\,d\eta}{\exp.\left[\frac{c}{\kappa\tau}\,(p^2+m_\pi{}^2c^2)^{\frac{1}{2}}-\lambda xp\eta\right]-1} \tag{1}$$

where $b_- = 3$. Similarly the number of κ-mesons in a volume element of phase space,

$$dN_\kappa = \frac{Mc^2 b_\mp}{2\pi\hbar^3 W}\,\frac{(R^2-x^2)\,dx\,p^2\,dp\,d\eta}{\exp.\left[\frac{c}{\kappa\tau}\,(p^2+m_\kappa{}^2c^2)^{\frac{1}{2}}-\lambda xp\eta\right]\mp 1}, \tag{2}$$

where $b_+ = 8$. In equation (2) the minus sign refers to spin 0 and the plus sign to spin $\frac{1}{2}$ for κ-mesons.

We obtain the total number of π-mesons and κ-mesons by integrating (1) and (2) over all momenta p from 0 to ∞, over x from $-R$ to $+R$ and over η from -1 to $+1$. These integrals as well as other integrals appearing in this paper are evaluated by expanding the integrand in a double infinite series as shown in the Appendix. The integrals can be expressed in the form of infinite series, the terms of which are themselves infinite series. But all the series converge rapidly. The expressions for the total numbers of π-mesons and κ-mesons are then

$$N_\pi = b_-\,\frac{Mc^2}{2\pi W}\,\frac{1}{a_\pi{}^3}\,h_-(a_\pi,\rho) \tag{3}$$

$$N_\kappa = b_\mp\,\frac{Mc^2}{2\pi W}\,\frac{1}{a_\pi{}^3}\,h_\mp(a_\kappa,\rho), \tag{4}$$

where

$$\rho = \frac{\lambda R\kappa\tau}{c},\quad a_\pi = \frac{m_\pi c^2}{\kappa\tau},\quad a_\kappa = \frac{m_\kappa c^2}{\kappa\tau};$$

the functions $h_-(a,\rho)$ and $h_+(a,\rho)$ as well as other functions appearing below are given in the Appendix.

The total energy W of the particles is obtained by multiplying (1) by $c(p^2 + m_\pi{}^2c^2)^{\frac{1}{2}}$ and (2) by $c(p^2 + m_\kappa{}^2c^2)^{\frac{1}{2}}$, adding the resulting expressions and integrating as before. We get

$$\left(\frac{W}{Mc^2}\right)^2 = \frac{1}{3\pi}\left(\frac{m_\pi}{M}\right)\frac{1}{a_\pi{}^4}[b_- f_-(a_\pi, \rho) + b_\mp f_\mp(a_\kappa, \rho)] \qquad (5)$$

Finally one obtains the total z-component of angular momentum of the particles by multiplying (1) and (2) by $xp\eta$ and adding and integrating. By equating the total angular momentum of the nucleons corresponding to the average value of the impact parameter to the total angular momentum of the liberated particles, we have

$$\frac{WR}{2c} = \frac{Mc^2}{2\pi\hbar^3 W}\left(\frac{\kappa\tau}{c}\right)^4 R^4 [b_- g_-(a_\pi, \rho) + b_\mp g_\mp(a_\kappa, \rho)] \qquad (6)$$

Using (5) in (6) we obtain after some transposition of terms

$$\frac{3}{\sqrt{2}}\frac{f_1(\rho)}{f_2(\rho)} = \frac{1}{\sqrt{2}} - \frac{3}{\sqrt{2}}\frac{b_- a_\pi{}^2 I_-{}^{(2)}(a_\pi) + b_\mp a_\kappa{}^2 I_\mp{}^{(2)}(a_\kappa)}{b_- I_-{}^{(1)}(a_\pi) + b_\mp a_\kappa{}^2 I_\mp{}^{(1)}(a_\kappa)}\frac{h_2(\rho) - \sqrt{2}\,h_1(\rho)}{f_2(\rho)}, \qquad (7)$$

where the functions $f_1(\rho)$ and $f_2(\rho)$ are the same as in Fermi's paper; $h_1(\rho)$, $h_2(\rho)$, $I^{(1)}(a)$ and $I^{(2)}(a)$ are defined in the Appendix. When $a_\pi = a_\kappa = 0$ equation (7) simply reduces to

$$\frac{3f_1(\rho)}{2f_2(\rho)} = \frac{1}{\sqrt{2}}. \qquad (8)$$

Actually the value of ρ determined from (7) differs very little from that determined from (8). Conversely, a given value of ρ can be considered to determine 'a certain' value of the impact parameter through (6), if $R/\sqrt{2}$ is replaced by r. Consequently we use a constant value for ρ throughout, namely 0·959.

The simplest procedure to obtain numerical values for the ratio N_κ/N_π at different primary energies is to assume certain values for a_π (which is just a number), the corresponding values of a_κ being obtained by multiplying a_π by $\frac{m_\kappa}{m_\pi}$. The primary energy corresponding to a set of values of a_π and a_κ is determined from (5) while expressions (3) and (4) give the numbers of π-mesons and κ-mesons. The Tables I and II below, are prepared in this manner. The ratio N_κ/N_π is calculated in Table I on the assumption that the κ-mesons has a spin 0 and a statistical weight 3 and in Table II, on the assumption of its spin being $\frac{1}{2}$ and statistical weight 8. The mass of the

TABLE I

$\kappa\tau/m_\pi c^2$	W'/Mc^2	N_π	N_κ	N_κ/N_π (Charged)
1	5·37	1·73	·225	0·13
2	$1·24\times10^2$	3·31	1·58	0·48
3	$7·04\times10^2$	5·0	3·4	0·68
5	$5·47\times10^3$	8·17	6·86	0·84
8	$3·68\times10^4$	13·0	12·1	0·93
10	$9·0\times10^4$	16·28	15·52	0·95

TABLE II

$\kappa\tau/m_\pi c^2$	W'/Mc^2	N_π	N_κ	N_κ/N_π (Charged)
1	7·2	1·5	0·514	0·26
2	$1·98\times10^2$	2·62	3·14	0·9
3	$1·23\times10^3$	3·78	6·02	1·2
5	$9·23\times10^3$	6·3	11·8	1·4
8	$6·15\times10^4$	10	20·2	1·5
10	$1·5\times10^5$	12·6	25·6	1·52

κ-meson is assumed to be 1,300 m_e and that of π-meson 280 m_e. The energy of the primary in the laboratory system is denoted by W'.

The results of Tables I and II favour the assumption of spin 0 and statistical weight 3 for κ-mesons.

It is a pleasure to express my thanks to Professor H. J. Bhabha for suggesting this problem to me and to Professor B. Peters for many helpful discussions concerning this work.

APPENDIX

We shall show below the method of evaluating the integral for the number of particles, the method being similar for other integrals.

$$N = A\int_{-R}^{+R}(R^2 - x^2)\,dx\int_{-1}^{+1}d\eta\int_{0}^{\infty}\left[\exp.\left\{\frac{c}{\kappa\tau}\,(p^2+m^2c^2)^{\frac{1}{2}}-\lambda x\eta p\right\}\mp 1\right]^{-1}p^2dp$$

$$= A\left(\frac{\kappa\tau}{c}\right)^3\int_{-R}^{+R}(R^2 - x^2)\,dx\int_{-1}^{+1}d\eta\int_{0}^{\infty}\frac{y^2dy}{\exp.\,[\sqrt{y^2+a^2}-\zeta y]\mp 1},$$

where

$A = \dfrac{Mc^2}{2\pi\hbar^2W}\,b_{\mp}$, $y = \dfrac{cp}{\kappa\tau}$, $a = \dfrac{mc^2}{\kappa\tau}$, $\zeta = \dfrac{\rho\eta x}{R}$ and $\rho = \dfrac{\lambda\kappa\tau R}{c}$. Now let $u = \sqrt{y^2+a^2} - \zeta y$. Substituting for y in terms of u, above, we get

$$N = A\left(\frac{\kappa\tau}{c}\right)^3\int_{-R}^{+R}dx\,(R^2 - x^2)\,\frac{R}{\rho x}\int_{-\frac{\rho x}{R}}^{+\frac{\rho x}{R}}\frac{d\zeta}{(1-\zeta^2)^3}\int_{a}^{\infty}\frac{du}{e^u\mp 1}$$

$$\left\{2u\zeta^2\sqrt{u^2-a^2(1-\zeta^2)} + \frac{u\,(u^2-a^2)+u\,(u^2+a^2)\,\zeta^2}{\sqrt{u^2-a^2(1-\zeta^2)}}\right\}$$

$$= A\left(\frac{\kappa\tau}{c}\right)^3\int_{-R}^{+R}dx\,(R^2 - x^2)\,\frac{R}{\rho x}\int_{a}^{\infty}\frac{du}{e^u\mp 1}\int_{-\frac{\rho x}{R}}^{+\frac{\rho x}{R}}\frac{d\zeta}{(1-\zeta^2)^3}$$

$$\left\{2u\zeta^2\sqrt{u^2-a^2}\,(1-\zeta^2) + \frac{u\,(u^2-a^2)+u\,(u^2+a^2)\,\zeta^2}{\sqrt{u^2-a^2(1-\zeta^2)}}\right\}$$

$$= 2A\left(\frac{\kappa\tau}{c}\right)^3\int_{-R}^{+R}dx\,(R^2 - x^2)\int_{a}^{\infty}du\,\frac{u^2\sqrt{1-\dfrac{a^2}{u^2}\left(1-\dfrac{\rho^2x^2}{R^2}\right)}}{e^u\mp 1}$$

$$= 2A\left(\frac{\kappa\tau}{c}\right)^3\frac{R^3}{\rho^3}\int_{1-\rho^2}^{1}\left(\frac{1}{\xi}-\frac{1-\rho^2}{\xi^2}\right)\frac{d\xi}{\sqrt{1-\xi}}\sum_{n=1}^{\infty}(\pm 1)^n\int_{a}^{\infty}du\,e^{-nu}$$

$$\left(u^2 - \frac{a^2}{2}\,\xi - \frac{a^4}{8}\,\frac{\xi^2}{u^2} - \frac{a^6}{16}\,\frac{\xi^3}{u^4} - \ldots.\right)$$

where we have put $\xi = 1 - \dfrac{\rho^2x^2}{R^2}$ and expanded $(1 \mp e^{-u})^{-1}$ and $\left(1 - \dfrac{a^2}{u^2}\,\xi\right)$, by the Binomial Theorem. Again, changing the variable from u to v by the substitution $u = v + a$ we have

$$N = 2A\left(\frac{\kappa\tau}{c}\right)^3 \frac{R^3}{\rho^3}\int_{1-\rho^2}^{1}\left(\frac{1}{\xi} - \frac{1-\rho^2}{\xi^2}\right)\frac{d\xi}{\sqrt{1-\xi}}\sum_{\eta=1}^{\infty}(\mp 1)^n e^{-na}\int_0^{\infty} dv\, e^{-na}$$

$$\left[(v+a)^2 - \frac{a^2}{2}\xi - \frac{a^4}{8}\frac{\xi^2}{(v+a)^2} - \ldots.\right]$$

$$= \frac{Mc^2}{2\pi\hbar^3 W} h_{\mp} R^3\left(\frac{\kappa\tau}{c}\right)^3 h_{\mp}(a,\rho)$$

where

$$h_{\mp}(a,\rho) = f_3(\rho)\sum_{n=1}^{\infty}(\pm 1)^n\left(\frac{2}{n^3} + \frac{2a}{n^2} + \frac{a^2}{n}\right) - a^2 h_3(\rho)\sum_{n=1}^{\infty}(\pm 1)^n\frac{e^{-na}}{n}$$

$$- \frac{a^4}{3}\sum_{n=1}^{\infty}(\pm 1)^n\left[\frac{e^{-na}}{a} - n\,Ei(an)\right] - \ldots.$$

and

$$Ei(x) = \int_{\infty}^{x}\frac{e^{-t}}{t}\,dt$$

$$f_3(\rho) = \frac{1+\rho^2}{\rho^3}\log\frac{1+\rho}{1-\rho} - \frac{2}{\rho^2}$$

$$h_3(\rho) = \frac{2}{\rho^2} - \frac{1-\rho^2}{\rho^3}\log\frac{1+\rho}{1-\rho}.$$

The other expressions for the energy and angular momentum can be calculated similarly, and we get the expressions (5) and (6) given in the text where

$$f_{\mp}(a,\rho) = I_{\mp}^{(1)}(a) f_3(\rho) - 3a^2 I_{\mp}^{(2)}(a) h_3(\rho) - \frac{a^4}{2} I_{\mp}^{(3)}(a) - \ldots.$$

$$g_{\mp}(a,\rho) = I_{\mp}^{(1)}(a) f_1(\rho) - 2a^2 I_{\mp}^{(2)}(a) h_1(\rho) - \ldots.$$

and

$$I_{\mp}^{(1)}(a) = \sum_{n=1}^{\infty}(\pm 1)^n\left(\frac{6}{n^4} + \frac{6a}{n^3} + \frac{3a^2}{n^2} + \frac{a^3}{n}\right)e^{-na}$$

$$I_{\mp}^{(2)}(a) = \sum_{n=1}^{\infty}(\pm 1)^n\left(\frac{1}{n^2} + \frac{a}{n}\right)e^{-na}$$

$$I_{\mp}^{(3)}(a) = \sum_{n=1}^{\infty}(\pm 1)^n\, Ei(an)$$

Here $f_1(\rho)$ and $f_2(\rho)$ are the same functions as those in Fermi's paper, namely

$$f_1(\rho) = \frac{2}{\rho^3} + \frac{\frac{4}{3}\rho}{1-\rho^2} - \frac{1+\frac{1}{3}\rho^2}{\rho^4}\log\frac{1+\rho}{1-\rho}$$

$$f_2(\rho) = \frac{1}{\rho}\log\frac{1+\rho}{1-\rho} + \frac{2}{1-\rho^2}$$

while

$$h_1(\rho) = \frac{3-\rho^2}{2\rho^4}\log\frac{1+\rho}{1-\rho} - \frac{3}{\rho^3}$$

$$h_2(\rho) = \frac{1}{\rho^3}\log\frac{1+\rho}{1-\rho} - \frac{2}{\rho^2}$$

REFERENCES

E. Fermi .. *Prog. Theo. Phy.*, 1950, **5**, 570.

———— .. *Phy. Rev.*, 1951, **81**, 683.

Bristol Conference on V-Particles and Heavy Mesons, 1951.

Note added in Proof.—After the contents of this paper had been worked out we received a pre-publication copy of a paper on the same subject by V. Haber-Schaim and G. Yekutieli (*Phil. Mag.*, 1952, **43**, 997). The chief interest of our paper lies in the explicit expressions for the integrals which enable one to incorporate other types of particles, as and when the occasion arises. The values for the ratio n_K/n_π in this paper are slightly lower than the values given by Haber-Schaim and Yekutieli but it is not easy to see the reason for this as no details are given in their paper.

SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

Part XXI. Isomerisation of C-(6 or 8)-methyl-5: 7-dihydroxy Chromones

By S. K. Mukerjee, T. R. Seshadri, F.A.Sc., and S. Varadarajan

(From the Department of Chemistry, University of Delhi, Delhi)

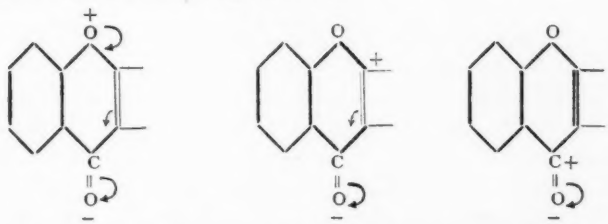
Received October 14, 1952

Mechanism of the isomeric change in hydroxy phloroglucinol derivatives

In earlier publications[1–6] have been discussed in detail the conditions of isomeric change from 5: 7: 8-hydroxy chromones and flavones (I) into the 5: 6: 7-hydroxy isomers (II). The change takes place in the presence of boiling hydriodic acid or hydrobromic acid and it is prevented by the presence of a hydroxyl or phenyl group in the 3-position.[3, 5] The reverse change, *i.e.*, from (II) to (I) does not take place.[7] The explanation of this isomeric change may be briefly given as follows: (i) In the case of 3-hydroxy or phenyl substituted compounds, the pyrone ring is stable and does not open. (ii) In other cases, the ring opening takes place and the subsequent ring closure involves a different but more active hydroxyl group. (iii) The influence of the 3-hydroxyl or 3-phenyl group is exerted by inhibiting the opening of the pyrone ring.

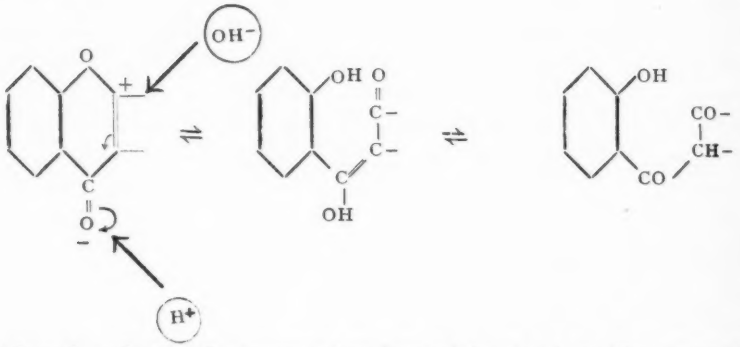
I $R=CH_3$ or C_6H_5 II

For detailed discussion, the main forms of the pyrone molecule can be represented by the following formulæ.

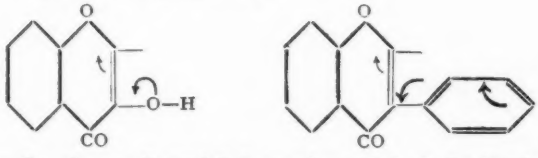


The electrophilic activity is mostly found in position 2. For example, the ring fission in alkaline solution can be formulated as being initiated by an

attack of this position by the nucleophilic reagent. Since boiling hydriodic acid brings about isomeric change, it should be accepted that in these cases the pyrone ring is capable of undergoing fission even in acid medium under these conditions. The change should be one of small degree and reversible so that when the system is cooled, only the pyrone is isolated. But this small degree reaction should be enough to bring about the isomeric change, since the alternative ring closure is favoured by the comparatively high reactivity of the alternative ortho hydroxyl group. It may be emphasised here that this isomeric change is a slow reaction and takes about two hours for completion.

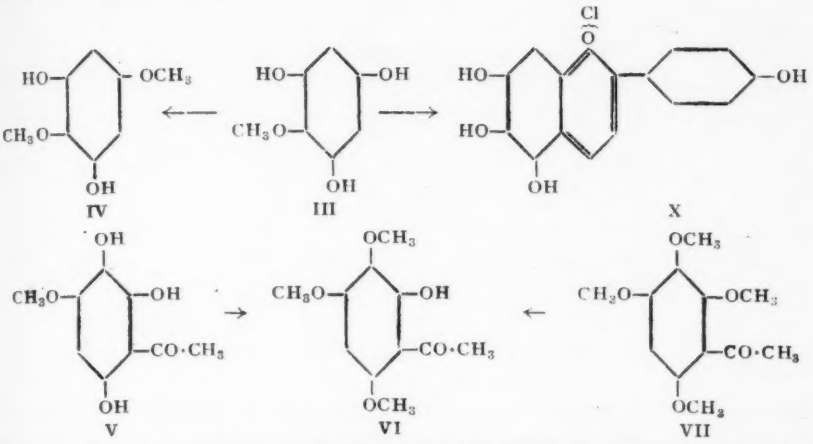


Hydroxyl and phenyl groups when located in the 3-position seem to act by increasing the availability of electrons in the 2-position. This will naturally reduce the already low electrophilic activity of this position in acid medium and thus prevent ring opening.

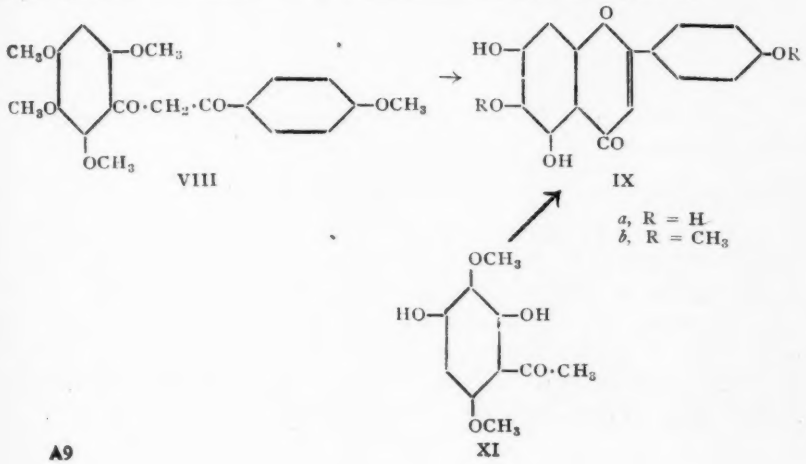


The reason for the preferential formation of 5:6:7-trihydroxy isomers is to be found in the greater reactivity of one of the two hydroxyl groups present ortho to the carbonyl group; it is located para to another hydroxyl (methoxyl) group. The greater reactivity of this hydroxyl group is independently established in several other reactions: (*a*) The methylation of iretol (III) has been shown to yield 1:3-dihydroxy-2:5-dimethoxy benzene (IV) and not the alternative 2:3-dimethoxy compound.[8] (*b*) Partial methylation of 2:3:6-trihydroxy-4-methoxy acetophenone (V) produces 2-hydroxy-3:4:6-trimethoxy acetophenone (VI).[9] (*c*) A similar behaviour is noticed in the demethylation of 2:3:4:6-tetramethoxy acetophenone (VII) which

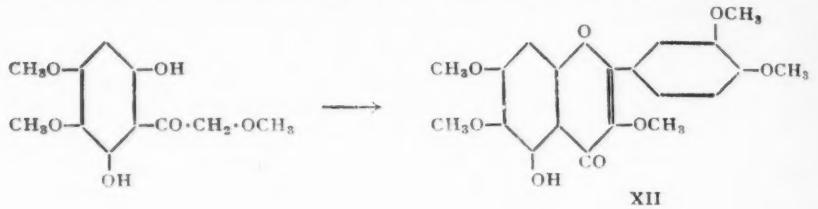
gives 2-hydroxy-3 : 4 : 6-trimethoxy acetophenone (VI) and not the isomeric 2-hydroxy-4 : 5 : 6-trimethoxy acetophenone[10] showing that the 6-methoxyl group is more stable.



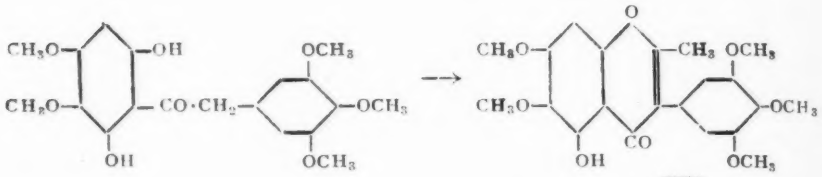
(*d*) A number of examples could be quoted from ring closure of various types. By heating 2 : 3 : 4 : 6 : 4′-pentamethoxy dibenzoyl methane (VIII) with hydriodic acid, scutellarein (IX *a*) is obtained as the product.[11] Similarly the condensation of iretol (III) with anisoyl acetaldehyde and subsequent demethylation of the product yields carajuretin hydrochloride (X).[8] The anisoylation of 2 : 4-dihydroxy-3 : 6-dimethoxy acetophenone (XI) using the Allan-Robinson procedure is accompanied by abnormal demethylation and the product is found to be scutellarein dimethyl ether (IX *b*).[12]



Further examples are provided by the syntheses of quercetagetin pentamethyl ether (XII)[13] and 2-methyl irigenin-7: 3′-dimethyl ether (XIII).[14]

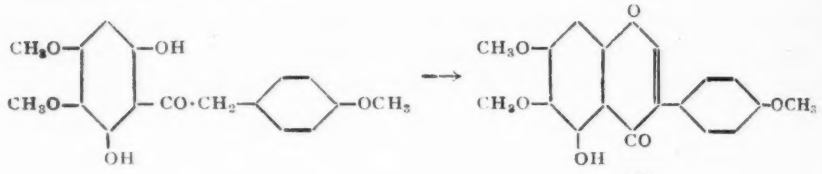


XII



XIII

Based on such results Baker and Robinson[14] have stated that " it appears a general rule that when a derivative of 1: 2: 3: 5-tetrahydroxy benzene undergoes ring closure, it is the hydroxyl in the position 5 which is concerned ". This conclusion has been further supported by the synthesis of tectorigenin dimethyl ether (XIV) from 2: 6-dihydroxy-4: 5: 4′-trimethoxy phenyl benzyl ketone (XV).[15]



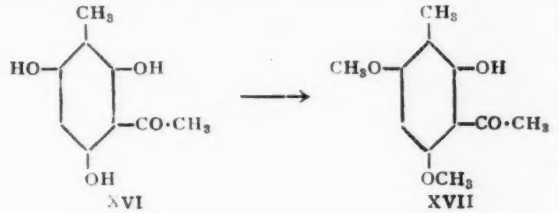
XIV

In all these cases the ring closure takes place in such a manner as to yield a compound of 5: 6: 7-trihydroxy type.

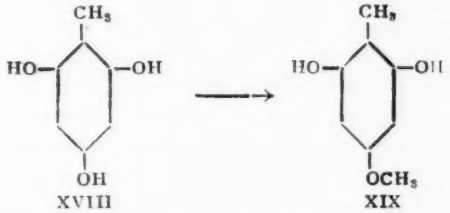
Isomeric change in C-methyl phloroglucinol derivatives

In the isomeric change from 5: 7: 8 to 5: 6: 7-hydroxy compounds it seemed probable that the 8-hydroxyl group may be playing some part in facilitating the opening of the pyrone ring. In order to test this point, the effect of substitution of a methyl group in this position would appear to be interesting. Actually compounds of this type having C-methyl groups in the condensed benzene ring have been recently isolated from *Eugenia caryophyllata*. From this source, Schmid and co-workers have obtained a

number of compounds which are closely related. These are eugenin (XXVIII),[16] eugenone (XXVI *b*),[17] eugenitin (XXV),[18] isoeugenitin (XXII *b*)[19] and isoeugenitol (XXII *a*).[20] Their constitutions were established by appropriate degradation reactions. They noticed that isoeugenitin methyl ether (XXI) could be demethylated with hydriodic acid to yield isoeugenitol (XXII *a*) without any isomeric change[21] whereas eugenitin (XXV) under the same conditions underwent isomeric change to form isoeugenitol.[18] This observation is of an extraordinary nature and the change is just the opposite of what happens with analogous trihydroxy compounds. Further it is not even in accordance with the behaviour of methyl phloroglucinol derivatives either in methylations or in reactions involving ring closure. In all these reactions a methyl group has the same effect as the hydroxyl group and it is the particular hydroxyl group which is para to the methyl group that is found to be more reactive. For example, the methylation of 2:4:6-trihydroxy-3-methyl acetophenone (XVI) yields 2-hydroxy-3-methyl-4:6-dimethoxy acetophenone (XVII).[22] Similarly methyl phloroglucinol (XVIII) gives the α-methyl ether (XIX).[22, 23] In the synthesis of eugenitin (XXV) starting from 2:4:6-trihydroxy-3-methyl acetophenone (XVI) it is this hydroxyl group which is para to the methyl group that is again reactive.[21] Hence the observation of Schmid and co-workers about the isomeric change appeared to be exceptional and seemed to require careful re-examination. Further several of the steps in the synthesis of eugenitin were not fully characterised by the earlier workers.



XVI XVII



XVIII XIX

Present work

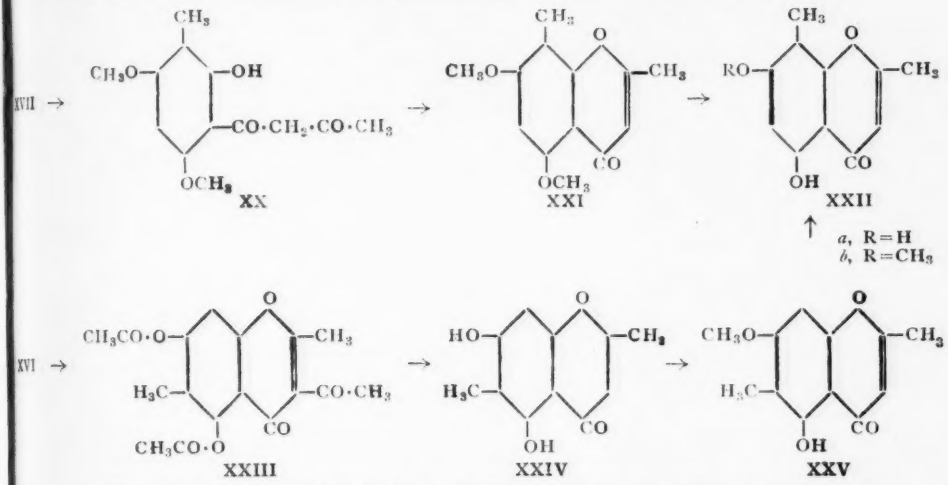
2-Hydroxy-3-methyl-4:6-dimethoxy acetophenone (XVII)[22] is converted into isoeugenitin methyl ether by way of the diketone (XX) according to

the method of Schmid and Bolleter.[21] These authors have reported that this chromone is dimorphic and the two forms melt at 132° and 174° respectively and that both are anhydrous. Both of them were obtained by these authors by sublimation under reduced pressure. It has now been found that when crystallised from dilute alcohol the compound is hydrated and is found to have a melting point of 96–97°. The anhydrous form could however be obtained by repeated dissolution of the hydrated compound in dry benzene and evaporation. This form melts at 174° agreeing with one of the forms reported by Schmid and Bolleter. Under these conditions, the crystal modification melting at 132° could not be obtained. On demethylation with aluminium chloride in benzene solution, the compound yields the normal product, 2: 8-dimethyl-5: 7-dihydroxy chromone (XXII *a*). This reagent is known to produce demethylation without any isomeric change.[1, 4, 6, 21] The product and its acetate agreed in all respects with isoeugenitiol and its acetate. The product obtained by treating 2: 8-dimethyl-5: 7-dimethoxy chromone with boiling hydriodic acid could not however be obtained easily pure by crystallisation. However, on acetylation, it yields an acetate which is found to be identical with 2: 8-dimethyl-5: 7-diacetoxy chromone and the product obtained on methylation with excess of dimethyl sulphate and potassium carbonate in acetone medium is found to be identical with 2: 8-dimethyl-5: 7-dimethoxy chromone thus clearly showing the absence of any rearrangement during this demethylation with hydriodic acid. On boiling isoeugenitiol (XXII *a*) with methyl iodide and potassium carbonate in acetone solution, a good yield of isoeugenitin (XXII *b*) agreeing with the natural product is obtained. Its acetate which has not been reported earlier has now been prepared.

The synthesis of eugenitin (XXV) itself has now been carried out on the same lines as those adopted by Schmid and Bolleter.[21] The starting material for this synthesis, 3-methyl phloracetophenone (XVI) was first made by the Hoesch condensation of C-methyl phloroglucinol with acetonitrile.[22] This is found to give only very poor yields of the ketone. Although the ketimine hydrochloride is formed in a good yield, during hydrolysis, considerable resinification takes place. It has now been found that 3-methyl phloracetophenone (XVI) could be obtained in nearly quantitative yield by the demethylation of 2-hydroxy-3-methyl-4: 6-dimethoxy acetophenone (XVII) with aluminium chloride in benzene solution. The product is easily isolated in the pure state and is identical with the ketone obtained by the method of Curd and Robertson.[22]

On heating 3-methyl phloracetophenone (XVI) with acetic anhydride and sodium acetate for 18 hours at 170–75°, 2: 6-dimethyl-3-acetyl-5: 7-

diacetoxy chromone (XXIII) is obtained which on boiling with aqueous sodium carbonate gives 2:6-dimethyl-5:7-dihydroxy chromone (XXIV). The properties of this substance as well as its diacetate are different from those of isoeugenitol (XXII *a*) and its diacetate respectively. By subsequent methylation with dimethyl sulphate and potassium carbonate in acetone solution, eugenitin (XXV) is obtained. Its acetate has the same melting point as reported by Schmid.[18] Heating eugenitin with hydriodic acid gives rise to a dihydroxy chromone identical with isoeugenitol as reported by Schmid.[18] This has now been confirmed by the preparation of the acetate also.

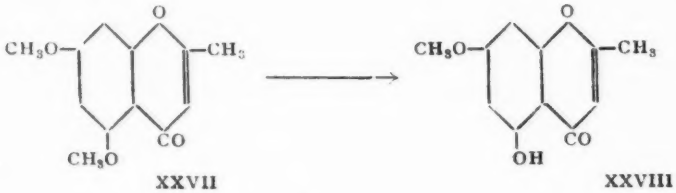


The observations of Schmid and Bolleter[18, 21] regarding the isomeric change have thus been confirmed. The very exceptional nature of this change has already been discussed. At present there is not sufficient data to explain this phenomenon. However it could be suggested as a possibility that the reactivity of the hydroxyl groups may differ under different conditions. Even though in methylations and chromone ring formation using acetic anhydride and sodium acetate, the hydroxyl para to the methyl may be more active, it may be just the reverse in the presence of boiling hydriodic acid. However this is peculiar to the C-methyl phloroglucinol derivatives and is not found in C-hydroxy phloroglucinol derivatives. Further investigation is in progress.

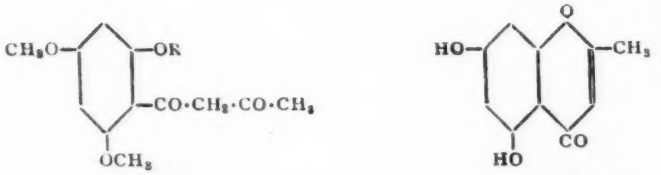
Synthesis of eugenin

In the reactivity of the hydroxyl groups of the condensed benzene ring, the isoflavone derivatives differ markedly from the corresponding flavones. This was explained by Aghoramurthy *et al.*[25] as due to the presence of the

phenyl group in the 3-position instead of the 2-position. As a consequence it is easy to effect partial demethylation of methyl ethers of isoflavones using even hydriodic acid and obtain the 7-methyl ethers, *e.g.*, santal (XXX *a*),[26] prunetin (XXX *b*)[27] and isoformononetin (XXXI).[25] Similar conditions should prevail in the case of the simpler chromones in which the side phenyl group is absent. This has now been confirmed by carrying out the demethylation of 2-methyl-5 : 7-dimethoxy chromone (XXVII) using hydriodic acid at 115° for 30 minutes and a good yield of eugenin (XXVIII) is obtained. The required dimethyl ether (XXVII) was originally made by Mckenzie, Robertson and Whalley[22] by cyclising 2-hydroxy-4 : 6-dimethoxy-ω-acetyl acetophenone (XXVI *a*). This methyl ether has now been made by methylation of 2-methyl-5 : 7-dihydroxy chromone (XXIX) with dimethyl sulphate by the dry method.

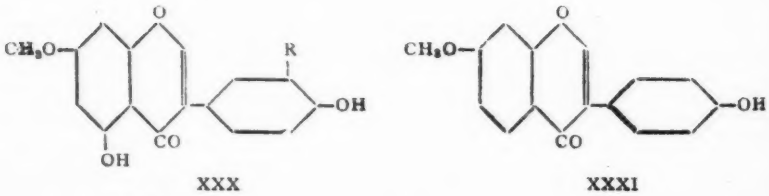


XXVII XXVIII



XXVI XXIX

a, R = H
b, R = CH_3



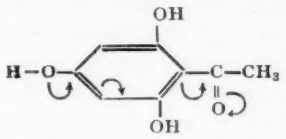
XXX XXXI

a, R = OH
b, R = H

In view of the reported nuclear methylation of genistein by means of methyl iodide and potassium carbonate in anhydrous acetone solution,[29] the reaction has now been carried out using 2-methyl-5: 7-dihydroxy chromone (XXIX). However no nuclear methylation takes place and a good yield of eugenin is again obtained. There seems to be therefore no need for using the more costly and difficultly available reagent diazomethane for the synthesis of this substance as was originally done by Meijer and Schmid.[16]

The theory of reactivity of C-hydroxy (methoxy) and C-methyl phloroglucinol derivatives

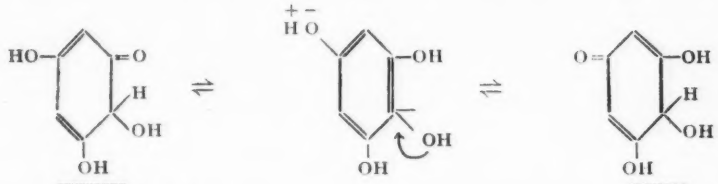
No explanation seems to have been offered so far for the marked difference in reactivity of the hydroxyl groups in C-hydroxy (methoxy) phloroglucinol derivatives discussed in the earlier paragraphs. However a detailed study has been made of phloracetophenone and similar compounds. In these, the para hydroxyl is definitely far more reactive in alkylations[30] as well as in benzoylation[31] as compared with ortho hydroxyl groups. This is obviously due to the effect of the C = O group which produces maximum positive charge on the nuclear position para to it and thus makes the para hydroxyl group most acidic and most reactive.



It is significant that even a hydroxyl or methoxyl group produces the same effect as a carbonyl group. A number of examples of C-hydroxy and C-methoxy phloroglucinol derivatives have already been given in which a hydroxyl para to these substituents is found to be more reactive as compared with the ortho hydroxyl group. These substituents, unlike the carbonyl, act as electron sources and hence a different type of mechanism should be involved.

It seems to be reasonable to consider that all phenolic compounds exhibit tautomerism and exist to some extent in the isomeric carbonyl forms; the facility with which this tautomerism is possible determines their reactivity. This is supported by the behaviour of 1: 4-dihydroxy-2-methyl naphthalene when it undergoes substitution with phytyl group leading to the synthesis of vitamin K.[32] Hydroxyl and similar electron donating groups can create nucleophilic activity on the carbon atom to which they are linked and they may be expected to help this tautomerism. Of the possible

structures, the para quinonoid form (XXXII) is obviously more easily produced than the isomeric ortho quinonoid type (XXXIII) and hence the para hydroxyl would be more reactive than the one at the ortho position.



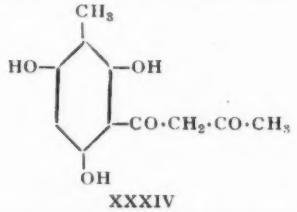
XXXIII XXXII

Extending this consideration to the ketones derived from C-hydroxy and C-methoxy phloroglucinol, the most reactive hydroxyl naturally should be the one para to the C = O group. When this is protected by methylation, subsequent reaction takes place involving the hydroxyl ortho to the carbonyl and para to the C-hydroxyl or C-methoxyl group.

As already mentioned, the influence of the methyl group in C-methyl phloroglucinol and C-methyl phloracetophenone derivatives in methylations and chromone ring closure is very similar to that of a hydroxyl or methoxyl group and the explanation given above should therefore be extended to these cases also; a methyl group is also an electron source though not so efficient as a hydroxyl or methoxyl group. But the behaviour of C-methyl chromones under the influence of boiling hydriodic acid is exceptional and other factors, hitherto un-understood, may be involved. This requires further investigation using related compounds before it could be fully understood.

Biogenesis

Schmid and Bolleter[20] have suggested that eugenitin and isoeugenitol can arise in the plant from the hypothetical intermediate, 2 : 4 : 6-trihydroxy-3-methyl-ω-acetyl acetophenone (XXXIV). They consider that the ring closure can take place in two ways giving rise to a 6 or 8-methyl chromone.



XXXIV

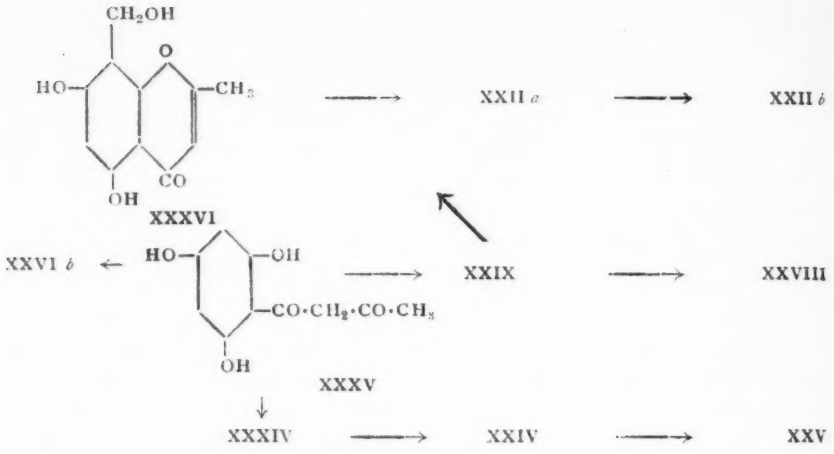
There is difficulty in accepting this as a biogenetic possibility. Taking laboratory analogy, under one set of conditions, only one isomer seems to

be formed. When 2:4:6-trihydroxy-3-methyl-ω-acetyl acetophenone (XXXIV) is subjected to ring closure under mild acid conditions, the 6-hydroxyl will be more reactive and only the 6-C-methyl chromone will be obtained and this may be expected to be the normal reaction in the plant. It is not reasonable to expect the drastic conditions of boiling hydriodic acid under the conditions of plant life. Hence a different process should be prescribed for the formation of the 8-methyl compounds, isoeugenitol (XXII *a*) and isoeugenitin (XXII *b*). Further, the occurrence of eugenone (XXVI *b*) and eugenin (XXVIII) in the same plant cannot be explained assuming the above hypothetical intermediate (XXXIV) of Schmid and Bolleter.

A more comprehensive scheme has therefore to be considered. For this purpose, a near derivative of eugenone, nor-eugenone (XXXV) offers a better starting point. By complete O-methylation, it would yield eugenone (XXVI *b*). In this case even the resistant 2-hydroxyl group of the diketone (XXXV) gets methylated and hence a fairly powerful mechanism should be available for this purpose. Ring closure of this diketone (XXXV) would give nor-eugenin (XXIX) which on subsequent partial methylation would give eugenin (XXVIII).

The other three compounds contain C-methyl groups; of these, isoeugenitol is the simplest, without any O-methylation in it. For its biogenesis, nor-eugenone (XXXV) is again the simpler starting point; chromone ring closure may be considered to take place first followed by nuclear methylation in the 8-position. Laboratory experiments indicate that the 8-position in chromones is the reactive one and they combine with hexamine to produce the corresponding 8-aldehydes[33] which can undergo reduction to the 8-methyl compounds.[34] A similar process could be postulated for the biogenesis of the 8-methyl chromones in the plant, the necessary important intermediate being a chromone containing a carbinol group in the 8-position (XXXVI). In the above nuclear methylation, as in many others of the same type, formaldehyde should be considered to be the normal methylating agent, the initial stage being a carbinol undergoing subsequent reduction to a C-methyl.[35] Subsequent ether formation could yield isoeugenitin (XXII *b*) from isoeugenitol (XXII *a*), the more resistant 5-hydroxyl being left free.

For the evolution of eugenitin (XXV), nor-eugenone (XXXV) may be considered to undergo nuclear methylation to (XXXIV) followed by ring closure and subsequent partial etherification. This is in accordance with laboratory analogy as already shown earlier. Partial methylation that follows could methylate the more reactive 7-hydroxyl group.



EXPERIMENTAL

2 : 8-*Dimethyl*-5 : 7-*dimethoxy chromone* (XXI)

2-Hydroxy-3-methyl-4 : 6-dimethoxy-ω-acetyl acetophenone[21] (1·6 g.) was dissolved in absolute alcohol (25 c.c.) and the solution refluxed with 2 drops of concentrated hydrochloric acid for 30 minutes on a water-bath. The mixture was concentrated to 10 c.c. and diluted with hot water (100 c.c.) and allowed to cool when crystals of 2 : 8-dimethyl-5 : 7-dimethoxy chromone separated. On recrystallisation from dilute alcohol, it was obtained in the form of fine colourless needles and rectangular rods melting at 96–97°. Yield 1·4 g. (Found: C, 60·2; H, 6·6. $C_{13}H_{14}O_4$, $1\frac{1}{2}$ H_2O requires C, 59·8; H, 6·5%).

This sample (0·1 g.) was dissolved in dry benzene (5 c.c.) and the benzene evaporated off. The process was repeated thrice. The residue was crystallised from a mixture of benzene and petroleum ether, when it came out as colourless prisms melting at 174° (Found: C, 67·1; H, 6·3; $C_{13}H_{14}O_4$ requires C, 66·7; H, 6·0%). When this sample was crystallised again from dilute alcohol, it had a m.p. 96–97°.

Schmid and Bolleter[21] carried out this cyclisation using alcoholic sulphuric acid and give melting points 132° and 174°. Both these samples were obtained by them by vacuum sublimation and were anhydrous.

2 : 8-*Dimethyl*-5 : 7-*dihydroxy chromone* (*Isoeugenitol*) (*XXII a*)

(i) To a solution of 2 : 8-dimethyl-5 : 7-dimethoxy chromone (1 g.) in dry benzene (20 c.c.) cooled to 0°, anhydrous aluminium chloride (3 g.) was

added in small lots with shaking. The aluminium chloride complex began to separate immediately. After the addition, the mixture was heated under reflux on a water-bath for 2 hours. Benzene was then distilled off and the residual complex decomposed by the addition of ice (30 g.) and hydrochloric acid (4 c.c.). The precipitate was filtered off and after drying, was crystallised from a mixture of alcohol and ethyl acetate. 2: 8-Dimethyl-5: 7-dihydroxy chromone separated as pale yellow rectangular prisms melting at 236–37°. Yield 0·8 g.

The diacetate was prepared by heating the chromone (0·25 g.) with acetic anhydride (5 c.c.) and a few drops of pyridine at 140° for 2 hours. It crystallised from alcohol as colourless thick rectangular plates melting at 150–51° (Found: C, 62·2; H, 5·1; $C_{15}H_{14}O_6$ requires C, 62·0; H, 4·9%). Schmid and Bolleter[21] give same m.p.

(ii) 2: 8-Dimethyl-5: 7-dimethoxy chromone (1 g.) was dissolved in acetic anhydride (25 c.c.) and the solution was cooled in an ice-bath. Hydriodic acid (25 c.c., d., 1·7) was then added cautiously with stirring and the mixture heated in an oil-bath at 140° for 2 hours. It was then cooled and diluted with a saturated aqueous solution of sodium bisulphite. After 12 hours, the yellow precipitate was collected, washed with water and dried. On crystallisation from a mixture of alcohol and ethyl acetate, it was obtained as pale yellow rectangular prisms melting at 220–30°. It did not crystallise readily from alcohol but yielded a crystalline acetate and methyl ether more easily. It gave a blue colour with ferric chloride in alcoholic solution. It was easily soluble in alcohol and sparingly soluble in ethyl acetate.

The acetate prepared by the acetic anhydride-pyridine method had a m.p. 150-51° and was in every way identical with 2: 8-dimethyl-5: 7-diacetoxy chromone described in (i) above.

Remethylation

The dihydroxy-dimethyl chromone (0·4 g.) obtained by the hydriodic acid demethylation above, was dissolved in dry acetone (100 c.c.) and the solution refluxed on a water-bath for 20 hours with dimethyl sulphate (0·8 c.c.) and anhydrous potassium carbonate (4 g.). The potassium salts were filtered off and then washed with warm acetone twice. Acetone was distilled off from the combined filtrate and the residue treated with water (100 c.c.). On setting aside for two days, some solid separated. It was filtered and crystallised thrice from dilute alcohol when it was obtained in the form of fine colourless needles and long rectangular rods melting at 96–97°. It did not give any colour with ferric chloride in alcoholic solution and a mixed

melting point with 2: 8-dimethyl-5: 7-dimethoxy chromone (XXI) described earlier was not depressed.

2: 8-*Dimethyl-5-hydroxy-7-methoxy chromone* (*Isoeugenitin*) (*XXII b*)

2: 8-Dimethyl-5: 7-dihydroxy chromone (0·42 g.) was dissolved in dry acetone (150 c.c.). Methyl iodide (0·5 c.c.) and anhydrous potassium carbonate (2·5 g.) were added and the mixture refluxed for 3 hours. The potassium salts were filtered off and washed with acetone. The crystalline residue left on distillation of the solvent, was recrystallised from alcohol twice. It came out as colourless needles melting at 148–49°. Schmid,[18] who carried out this methylation with excess of diazomethane in methyl alcohol at — 10° gives m.p. 147–48°. It gave a blue colour with alcoholic ferric chloride (Found: C, 65·2; H, 5·6. $C_{12}H_{12}O_4$ requires C, 65·5; H, 5·5%).

The acetate, prepared by acetylation with acetic anhydride and pyridine, crystallised from dilute alcohol as colourless rectangular rods and prisms and melted at 136–37° (Found: C, 64·4; H, 5·5; $C_{14}H_{14}O_5$ requires C, 64·1; H, 5·4%).

2: 4: 6-*Trihydroxy-3-methyl acetophenone* (*XVI*)

2-Hydroxy-3-methyl-4: 6-dimethoxy acetophenone (XVII)[22] (4 g.) was dissolved in dry benzene (35 c.c.) and well powdered, anhydrous aluminium chloride (12 g.) was added. The aluminium chloride complex separated out. The mixture was refluxed in a water-bath for 2 hours. Benzene was then distilled off completely and the residue cooled and treated with crushed ice and hydrochloric acid (20 c.c.). After two hours, the almost colourless precipitate was filtered, washed with water and treated with excess of aqueous sodium carbonate (10%). A small amount of undissolved matter was filtered off and the filtrate acidified. The colourless precipitate was collected. Yield 3·0 g., m.p. 208–10°. On crystallisation from boiling water, 3-methyl phloracetophenone was obtained as clusters of colourless needles melting at 211–12°. A mixed melting point with an authentic sample of the ketone prepared according to the method of Curd and Robertson[22] was not depressed.

2: 6-*Dimethyl-3-acetyl-5*: 7-*diacetoxy chromone* (*XXIII*)

An intimate mixture of 2: 4: 6-trihydroxy-3-methyl acetophenone (5 g.) and fused sodium acetate (12 g.) was heated with acetic anhydride (100 c.c.) at 150° for half an hour and then at 170–75° for 18 hours. The clear red solution was poured into crushed ice. The dark solid that separated on leaving overnight was filtered and washed with water. On maceration with

cold alcohol, the coloured impurities dissolved. The colourless solid was filtered, washed with cold alcohol and crystallised from the same solvent twice. 2: 6-Dimethyl-3-acetyl-5: 7-diacetoxy chromone was obtained in the form of colourless rectangular prisms melting at 159–61°. Yield 2·1 g. (Found: C, 63·0; H, 5·2. $C_{13}H_{12}O_5$ requires C, 62·9; H, 4·8%).

The mother liquors on concentration gave 2: 4: 6-triacetoxy-3-methyl acetophenone as a colourless crystalline solid (1·7 g.) which when recrystallised from alcohol had a m.p. 114–15°. Curd and Robertson[22] give m.p. 111° for this compound.

2: 6-*Dimethyl*-5: 7-*dihydroxy chromone* (*XXII*)

The above 3-acetyl compound (1·75 g.) was heated with 10% aqueous sodium carbonate (100 c.c.) under reflux for 2 hours. The solid slowly went into solution. The solution was filtered from any insoluble matter, cooled to 0° and acidified with ice-cold hydrochloric acid (1: 1) and then heated to 80° in a water-bath to coagulate the precipitated solid. The mixture was cooled to 0° again and the precipitate filtered off. Yield 1·0 g. When crystallised twice from alcohol, 2: 6-dimethyl-5: 7-dihydroxy chromone separated as colourless clusters of irregular prisms melting at 274–76° (decomp.). It gave a blue colour with alcohloic ferric chloride and was very sparingly soluble in alcohol (Found: C, 64·4; H, 5·2. $C_{11}H_{10}O_4$ requires C, 64·1; H, 4·9%).

The diacetate was prepared by heating the dihydroxy chromone with acetic anhydride and pyridine. When crystallised from alcohol twice, it was obtained in the form of clusters of colourless narrow rectangular plates melting at 200–02° (Found: C, 61·6; H, 4·6. $C_{15}H_{14}O_6$ requires C, 62·0; H, 4·9%).

2: 6-*Dimethyl*-5-*hydroxy*-7-*methoxy chromone* (*Eugenitin*) (*XXV*)

2: 6-Dimethyl-5: 7-dihydroxy chromone (XXIV) (0·9 g.) was dissolved in acetone (150 c.c.) and treated with freshly distilled dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (1·5 g.). The mixture was refluxed for 6 hours on a water-bath. Acetone was then distilled off and the potassium salts were dissolved in water (150 c.c.). The bluish solid was filtered and washed with water and crystallised from alcohol twice and then once from ethyl acetate, when 2: 6-dimethyl-5-hydroxy-7-methoxy chromone separated as colourless thick prisms melting at 161–62°. It gave a blue colour with alcoholic ferric chloride. Yield 0·4 g. Schmid[18] gives the m.p. of natural eugenitin as 162° (Found: C, 65·6; H, 5·4; $C_{12}H_{12}O_4$ requires C, 65·5; H, 5·5%).

The acetate prepared by the pyridine method, crystallised from alcohol as thin colourless rectangular plates melting at 176–77°. Schmid[18] gives the same m.p. for eugenitin acetate.

Demethylation

Eugenitin (0·27 g.) was heated with hydriodic acid (5 c.c., d., 1·7) for 2 hours in an oil-bath. The deep brown solution was poured into an ice-cold saturated aqueous solution of sodium bisulphite (75 c.c.). After 12 hours, the pale yellow solid was collected and washed with water. On crystallisation from alcohol twice, it was obtained as colourless thick rectangular plates melting at 236–37°. It was easily soluble in alcohol and the melting point did not rise on further crystallisation. A mixed melting point with an authentic sample of 2: 8-dimethyl-5: 7-dihydroxy chromone (XXII *a*) was not depressed.

The acetate, prepared by acetylation with acetic anhydride and pyridine, crystallised from alcohol and melted at 150–51° alone or when mixed with a sample of 2: 8-dimethyl-5: 7-diacetoxy chromone.

2-*Methyl*-5: 7-*dimethoxy chromone* (*XXVII*)

A solution of 2-methyl-5: 7-dihydroxy chromone (XXIX)[36] (1 g.) in dry acetone (100 c.c.) was heated with dimethyl sulphate (1·5 c.c.) and potassium carbonate (5 g.) for 15 hours. Acetone was then distilled off and water was added to the residue. After setting aside for two days, the solution was filtered through cotton and the filtrate extracted with ether. The brown oil which was left on distilling off the solvent from the ether solution, solidified on the addition of a small quantity of petroleum ether. It was filtered and crystallised from a mixture of ethyl acetate and petroleum ether when it separated as colourless plates melting at 124–25°. Yield 0·5 g. Mckenzie, Robertson and Whalley,[28] who obtained this compound by a different route give m.p. 124°.

2-*Methyl*-5-*hydroxy*-7-*methoxy chromone* (*Eugenin*) (*XXVIII*)

(i) 2-Methyl-5: 7-dihydroxy chromone[36] (0·7 g.) in acetone (100 c.c.) was mixed with methyl iodide (3 c.c.) and potassium carbonate (3 g.) and the mixture refluxed for 3 hours on a water-bath. The solvent was then distilled off and the residue treated with water. The undissolved methyl ether was filtered and crystallised from alcohol. It separated as colourless prisms melting at 118–19°. Yield 0·5 g. It gave a wine red colour with ferric chloride in alcoholic solution. Meijer and Schmid,[16] who carried out this methylation with diazomethane in methanol report the m.p. as 119–20°.

The acetate, prepared by acetylation with acetic anhydride and pyridine, crystallised from alcohol as colourless irregular prisms melting at 152–53°. Meijer and Schmid[16] give m.p. 152·5–153·5°.

(ii) 2-Methyl-5 : 7-dimethoxy chromone (XXVII) (0·35 g.) was dissolved in acetic anhydride (8 c.c.) and treated with hydriodic acid (12 c.c., d., 1·7). The mixture was heated in an oil-bath at 115° for 30 minutes and diluted with aqueous sodium bisulphite. The solution was neutralised with sodium bicarbonate. The precipitated solid was filtered and washed with water. It was insoluble in aqueous sodium carbonate. When crystallised from alcohol (Norit), it was obtained as colourless prisms melting at 118–19°. A mixed m.p. with the sample obtained in (i) above was not depressed.

Summary

A review of ring isomeric change of flavones and chromones is made as also of the reactivity of C-hydroxy phloroglucinol and C-hydroxy phloracetophenone derivatives in methylation, benzoylation and ring closure. The results are consistent showing the greater reactivity of a hydroxyl group of the quinol unit as compared with that of the catechol unit. A tentative explanation is given.

A synthetic study has been made of the chromones of *Eugenia caryophyllata*. All the intermediates in the synthesis of eugenitin have now been isolated and fully characterised. A convenient route for the preparation of the starting material for this synthesis, *viz.*, 3-methyl phloracetophenone has now been found. Two new syntheses of eugenin are also recorded. The observation of Schmid and Bolleter that eugenitin (6-methyl) undergoes change into isoeugenitol (8-methyl) when demethylated with boiling hydriodic acid and that isoeugenitin methyl ether (8-methyl) does not undergo isomeric change under the same conditions, is confirmed. This is the reverse of what has been observed in the case of C-hydroxy phloracetophenone derivatives. Further it is extraordinary because C-methyl phloroglucinol and C-methyl phloracetophenone behave like the C-hydroxy (methoxy) compounds in methylations and chromone ring closure.

An attempt has been made to develop a comprehensive scheme of biogenesis which includes all the five components occurring in *Eugenia caryophyllata*. The basic compound is taken to be nor-eugenone and all the stages are based on analogy with laboratory experiments.

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For recent literature on tautomerism in phenols, besides reference 32, see the following: *J.C.S.*, 1951, 1726 and 3265; 1952, 1855, 1858, 2446 and 2759.

SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

Part XXII. A Synthesis of 8-Methyl Genistein

BY T. R. SESHADRI, F.A.SC. AND S. VARADARAJAN

(From the Department of Chemistry, University of Delhi, Delhi)

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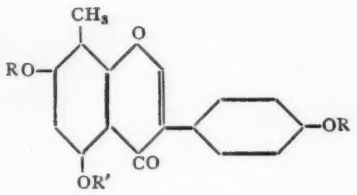
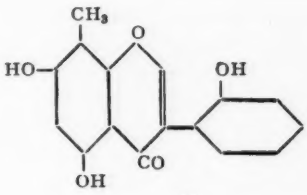
OKANO and BEPPU[1] reported the isolation of four isoflavones from soya beans. Three of these contain C-methyl groups and are the only examples of nuclear methylated isoflavones occurring in nature. They have deduced the constitutions of these three isoflavones as 8-methyl genistein (I *a*), 8-methyl isogenistein (II) and 8-methyl-5 : 4′-dihydroxy isoflavone (tatoin) (III) on the basis of degradation experiments.

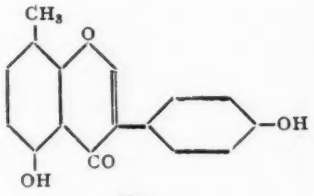


I



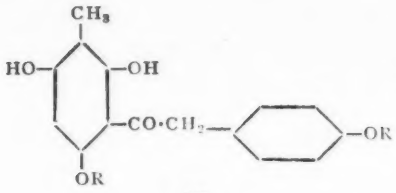
II

a, R = R′ = H
b, R = CH_3, R′ = H
c, R = R′ = CH_3

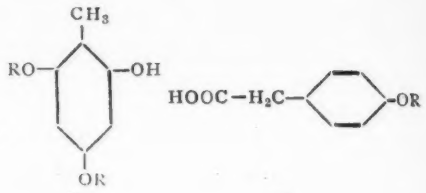


III

The constitution of (I *a*) was arrived at as follows. The analytical values and the molecular weight determination corresponded to the formula $C_{16}H_{12}O_5$. It yielded a triacetate, a dimethyl ether (I *b*) and a trimethyl ether (I *c*). On heating with alkali, it yielded formic acid and a tetrahydroxy ketone (IV *a*) which could be further degraded into C-methyl phloroglucinol (V *a*) and *p*-hydroxy phenyl acetic acid (VI *a*). The trimethyl ether (I *c*) on heating with alkali gave C-methyl phloroglucinol-α-dimethyl ether (V *b*) and *p*-methoxy phenyl acetic acid (VI *b*).



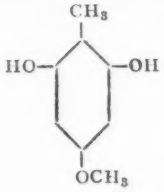
IV



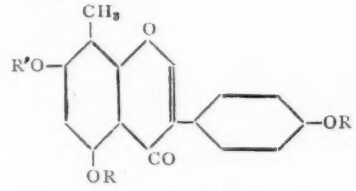
V VI

a, R = H
b, R = CH_3

A synthesis of 8-methyl genistein (I *a*) was also reported by Shriner and Hull.[2] The starting point for their synthesis was C-methyl phloroglucinol α-methyl ether (VII).[3] On Hoesch condensation with *p*-methoxy phenyl acetonitrile, it yielded 2 : 4-dihydroxy-3-methyl-6 : 4′-dimethoxy phenyl benzyl ketone (IV *b*) which on treatment with ethyl formate in presence of sodium gave rise to 7-hydroxy-8-methyl-5 : 4′-dimethoxy isoflavone (VIII *a*). The trihydroxy isoflavone (I *a*) obtained by the demethylation of this substance with hydriodic acid was found by the above authors to have the same melting point as natural 8-methyl genistein. The melting point of the acetate was also in agreement with that reported for the triacetate of 8-methyl genistein by Okano and Beppu.[1] However no direct comparison of the natural and synthetic samples was made.



VII



VIII

a, R = CH_3, R′ = H
b, R = H, R′ = CH_3

Elsewhere it has been pointed out that the origin of C-hydroxy and C-methyl groups in flavonoids have certain common features and some of the methods of nuclear oxidation are applicable for nuclear methylation also.[4, 13] These considerations could be conveniently tested using the naturally occurring C-methyl isoflavones as examples. Nuclear oxidation of isoflavones has been recently reported[5] and nuclear methylation has been under study. In the course of this work it was found necessary to prepare the C-methyl isoflavones by conventional methods for purposes of reference.

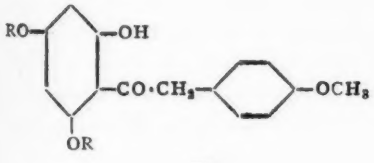
The preparation C-methyl phloroglucinol (V *a*) and its α-monomethyl ether (VII) used in the synthesis of Shriner and Hull[2] involve a number of

steps of decreasing yields. Direct nuclear methylation at the ketone stage seemed to offer a better method and a synthesis of 8-methyl genistein, based on such a reaction, has now been undertaken.

The ketone required for this purpose is 2:4:6-trihydroxy-4′-methoxy phenyl benzyl ketone (IX *a*). This was made earlier by Baker and Robinson[6] by the condensation of *p*-methoxy phenyl acetonitrile with phloroglucinol in presence of hydrogen chloride. The required nitrile has been prepared by a number of methods. A review of the earlier literature has been given by Shriner and Hull.[2]

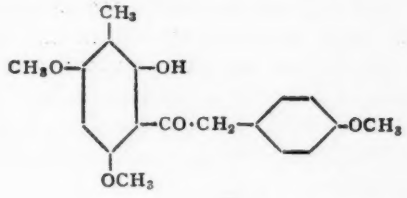
For the preparation of nitriles of this type, the method of Baker and Robinson[7] is of general applicability. The preparation of *p*-methoxy phenyl acetonitrile itself has been very briefly mentioned by Baker and Eastwood.[8] The details of the preparation are now described and further, *p*-methoxy phenyl pyruvic acid oxime, which was not described earlier has now been isolated and characterised.

The nuclear methylation of the ketone (IX *a*) has been carried out by heating an acetone solution of the ketone with excess of methyl iodide and potassium carbonate. Two products are obtained and these are separated by fractional crystallisation from methanol. The less soluble fraction which is obtained in an yield of 15% is 2-hydroxy-3-methyl-4:6:4′-trimethoxy phenyl benzyl ketone (X). That this compound has the constitution (X) and not the alternative (XI) is based on analogy with nuclear methylation of phloracetophenone.[3] It does not give any blue or green colour with nitric acid, showing that it contains another nuclear substituent. This conclusion is based on a detailed examination of this colour reaction by Rao and Seshadri[9] who have pointed out that a green or blue colour is given by ketones of type (XII) and that it is not answered by ketones of type (XIII). The more soluble fraction which gives blue colouration with nitric acid consists of 2-hydroxy-4:6:4′-trimethoxy phenyl benzyl ketone (IX *b*).[10, 11]

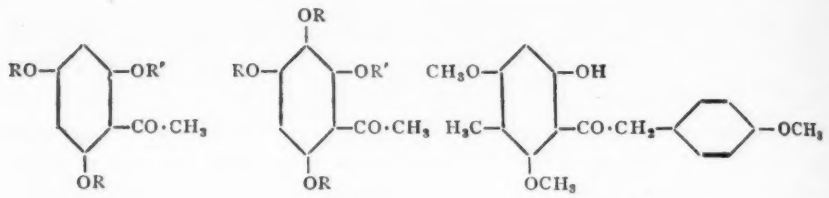


IX

a, R = H
b, R = CH_3



X



XII XIII XI

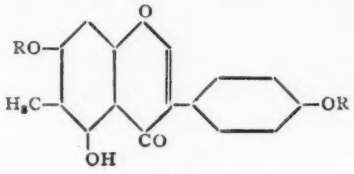
R = alkyl
R′ = H or alkyl

Treatment of the C-methyl ketone (X) with ethyl formate and sodium at 0°,[12] gives rise to a good yield of 8-methyl-5: 7: 4′-trimethoxy isoflavone (I *c*). It melts at 181–83°. Okano and Beppu[1] have however reported that 8-methyl genistein trimethyl ether had a melting point 154–55°. On demethylation with hydriodic acid, (I *c*) yields 8-methyl-5: 7: 4′-trihydroxy isoflavone (I *a*). This is found to be soluble in aqueous sodium carbonate showing that all the methoxyl groups including the one at the 7-position have been demethylated. When crystallised from dilute alcohol, it has a melting point 231–32°. The melting point does not rise on further crystallisation. Okano and Beppu[1] have however given the melting point of natural 8-methyl genistein as 298°. Shriner and Hull[2] have also reported the melting point of their synthetic sample to be 296–300°. Okano and Beppu[1] have stated that the natural isoflavone gives a violet or violet brown colour with alcoholic ferric chloride, whereas the synthetic product obtained in the present work gives a deep green colour with this reagent. Shriner and Hull[2] have not recorded this colour reaction with their substance.

It may be relevant to draw a comparison between 8-methyl genistein and other nuclear methylated chromones, in the ferric reactions exhibited by them. As described in an earlier publication,[13] all the C-methyl chromones from *Eugenia caryophyllata*, eugenitin, isoeugenitol and isoeugenitin give a blue colour with ferric chloride. In the absence of a C-methyl group, as exemplified by nor-eugenin and eugenin, only a wine red colour is developed. Genistein itself gives a pink ferric reaction and in the case of prunetin and genistein-7: 4′-dimethyl ether, it is brownish violet. Hence the production of a deep green colour with ferric chloride by the synthetic 8-methyl genistein is more in agreement with expectations for this structure than the violet or violet brown colour as given by the natural compound.

Besides the differences mentioned above, there is considerable difference in the melting points of the acetates also. The acetate prepared in this work

by the acetic anhydride-pyridine method on crystallisation from acetic acid melts at 213–15° whereas Okano and Beppu[1] and Shriner and Hull[2] report the melting point of the acetate to be 184° and 184–85° respectively. The acetate obtained in the present work has also been deacetylated with alcoholic hydrochloric acid. The resulting hydroxy compound has a melting point 231–32°, showing that it is a pure entity.



XIV

a, R = H

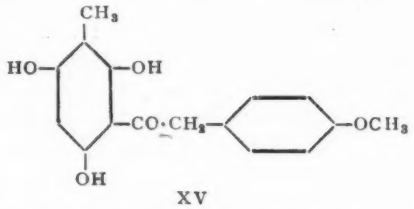
b, R = CH_3

There exists however a possibility that during the treatment of 8-methyl-5:7:4′-trimethoxy isoflavone (I *c*) with hydriodic acid, besides demethylation, isomeric change into 6-methyl-5:7:4′-trihydroxy isoflavone (XIV *a*) has also taken place. That this has not happened has been proved in two ways. The trimethyl ether (I *c*) has been demethylated with anhydrous aluminium chloride in benzene solution. It has recently been pointed out by Narasimhachari and Seshadri[14] that this reagent in benzene medium is capable of causing demethylation of the very resistant 7-methoxyl group in isoflavones. A large amount of the solvent has to be employed for the demethylation of (I *c*) due to the low solubility of the compound. That this reagent causes demethylation without isomeric change is well established.[15] The product is found to melt at 231–32° and is in every way identical with the trihydroxymethyl isoflavone obtained by demethylation of (I *c*) with hydriodic acid. Secondly, the hydriodic acid demethylation product has been methylated with excess of dimethyl sulphate and potassium carbonate in acetone solution. The resulting trimethyl ether is identical with the original 8-methyl-5:7:4′-trimethoxy isoflavone (I *c*). These two experiments definitely establish the absence of any rearrangement during demethylation. In an earlier publication[5] it has been shown that closely related isoflavones having a hydroxyl or methoxyl in the 8-position instead of a methyl group also do not undergo ring isomeric change when boiled with hydriodic acid.

The discrepancies are difficult to explain. The present synthesis seems to be quite unambiguous and hence it is possible that the natural compound does not have the constitution of 8-methyl genistein, as deduced by Okano

and Beppu.[1] But the discrepancies between the products of the present synthesis and those of Shriner and Hull[2] are more difficult to explain. The earlier method is certainly an acceptable one and hence there is difficulty in explaining the differences. Their method has therefore been reexamined and forms the subject-matter of a forthcoming publication.

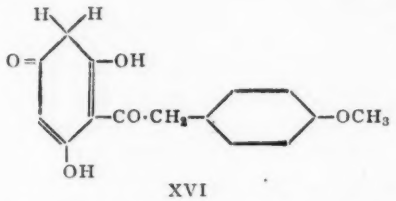
It is possible that during the preparation of the important intermediate, 2-hydroxy-3-methyl-4 : 6 : 4′-trimethoxy phenyl benzyl ketone (X) by nuclear methylation, instead of one C-methyl group, two such groups might have entered. Hence the above ketone (X) has now been prepared in another manner also, which leaves no doubt about its constitution. C-Methyl phloroglucinol (V *a*)[2] has been condensed with *p*-methoxy phenyl aceto-nitrile. A good yield of 2 : 4 : 6-trihydroxy-3-methyl-4′-methoxy phenyl benzyl ketone (XV) is obtained. This on methylation with two moles of dimethyl sulphate and excess of anhydrous potassium carbonate in acetone solution gives rise to 2-hydroxy-3-methyl-4 : 6 : 4′-trimethoxy phenyl benzyl ketone (X), identical in every way with the product obtained by nuclear methylation of 2 : 4 : 6-trihydroxy-4′-methoxy phenyl benzyl ketone (IX *a*). In the above methylation of the ketone (XV), it is the hydroxyl group in the 6-position (para to the methyl) that is methylated and not the one in the 2-position (ortho to the methyl group) follows from similar methylations of simpler ketones.[3, 16] It is also well known that dimethyl sulphate, unlike methyl iodide, does not cause any nuclear methylation and therefore the product of methylation of 2 : 4 : 6-trihydroxy-3-methyl-4′-methoxy phenyl benzyl ketone (XV) should contain only one C-methyl group and have the constitution (X).



XV

In this connection should be noted the observation of Curd and Robert-son[3] who found that treatment of C-methyl phloracetophenone with excess of methyl iodide gave only 2-hydroxy-3-methyl-4 : 6-dimethoxy aceto-phenone, *i.e.*, no further nuclear methylation took place. In the present work also, 2 : 4 : 6-trihydroxy-3-methyl-4′-methoxy phenyl benzyl ketone (XV) is found to yield the dimethyl ether (X) only, on heating with excess of methyl iodide and potassium carbonate in acetone solution and no fur-ther nuclear methylation takes place.

No explanation has been put forward so far for the absence of further nuclear methylation in C-methyl phloracetophenone derivatives. According to the mechanism of nuclear methylation of polyhydroxy carbonyl compounds,[17] this reaction requires the formation of the isomeric carbonyl form (XVI) and for this purpose a double bond should exist between the 3- and 4-positions of the ketone (IX *a*). This is facilitated by the fixation caused by the chelate ring. Consequently no double bond seems to function between the 4- and 5-positions, the 5-position does not get activated and no nuclear methylation takes place. This scheme assumes that the chelate structure is fixed and does not change from one position to another under the conditions of the experiment.



XVI

But this does not explain all observed facts. For example, C-methyl phloroglucinol (V *a*) yields the ketone (XV) which when methylated yields the same dimethyl ether (X) as obtained by the alternative method and not (XI). In (XV), ordinarily the more acidic hydroxyl group in the 6-position (para to the methyl group) could be expected to enter into chelation with the neighbouring carbonyl, in which case, it will be resistant to methylation. It is actually not so; the 6-hydroxyl group gets methylated easily and the 2-hydroxyl is again resistant and chelated. Obviously some other factor is playing an important part in the reactivity of (XV). This should be the tautomeric effect already explained.[13] The formation of the *p*-quinonoid structure being more favoured, the 6-hydroxyl group is not so readily available for chelation and hence the chelate ring is formed with the alternative 2-hydroxyl group.

Partial methyl ethers of 8-methyl genistein have also now been prepared. The technique of partial demethylation has been used for this purpose. Hydriodic acid under controlled conditions has been used for the demethylation of the 5- and 4′-methoxyl groups.[18] This reagent is preferable to hydrobromic acid which often causes resinification. Using it, 8-methyl-5: 7: 4′-trimethoxy isoflavone (I *c*) has been demethylated at 110° and the product, 8-methyl-5: 4′-dihydroxy-7-methoxy isoflavone (8-methyl prunetin) (VIII *b*) is obtained in a good yield. It is insoluble in aqueous sodium carbonate. It gives a brilliant green colour with alcoholic ferric chloride indicating the

presence of a free hydroxyl group at the 5-position. The diacetate has also been prepared by the acetic anhydride-pyridine method.

On methylation with one mole of dimethyl sulphate, 8-methyl prunetin (VIII *b*) yields its monomethyl ether, 8-methyl-5-hydroxy-7 : 4′-dimethoxy isoflavone (I *b*). Its properties are in agreement with this formulation. It exhibits a deep green ferric reaction which is comparable to the blue colour given by the corresponding chromone, isoeugenitin.[13]

A C-monomethyl-O-dimethyl genistein was described by Perkin and Horsfall,[19] who obtained it by the methylation of genistein with methyl iodide. This had a melting point 200–02° and it gave an initial violet colour changing to olive green with alcoholic ferric chloride.[6] The melting point of 8-methyl-5-hydroxy-7 : 4′-dimethoxy isoflavone (I *b*) obtained in the present work is 164–66°. The melting point of this substance and its ferric reaction are different from those reported for the methyl ether of Perkin and Horsfall.[19] Therefore the latter substance should be isomeric and not identical with (I *b*) and hence it should be 6-methyl-5-hydroxy-7 : 4′-dimethoxy isoflavone (XIV *b*) as suggested by Baker and Robinson.[6] It may however be mentioned that the 8-position is normally the reactive one in chromones. This nuclear methylation in which the 6-position gets substituted is therefore to be regarded as abnormal.

The structure assigned to the nuclear methylation product of genistein is supported by other considerations also. Perkin and Horsfall[19] demethylated this substance and obtained a C-methyl trihydroxy isoflavone, which had a melting point of 278°. This should therefore be different from 8-methyl genistein synthesised in the present work, which melts at 231–32°. Hence the trihydroxy methyl isoflavone of Perkin and Horsfall should be 6-methyl genistein (XIV *a*). A comparison of the melting points of these C-methyl genistein derivatives with those of the related C-methyl chromones[13] also supports the above conclusion. These are presented in the following table.

Substance	M.P.
2 : 8-Dimethyl-5-hydroxy-7-methoxy chromone (Isoeugenitin) ..	148–49°
2 : 6-Dimethyl-5-hydroxy-7-methoxy chromone (Eugenitin) ..	161–62°
2 : 8-Dimethyl-5 : 7-dihydroxy chromone (Isoeugenitol)	235–37°
2 : 6-Dimethyl-5 : 7-dihydroxy chromone (Eugenitol)	274–76°
8-Methyl-5-hydroxy-7 : 4′-dimethoxy isoflavone	164–66°
6-Methyl-5-hydroxy-7 : 4′-dimethoxy isoflavone	200–02°
8-Methyl-5 : 7 : 4′-trihydroxy isoflavone (8-Methyl genistein) ..	231–32°
6-Methyl-5 : 7 ; 4′-trihydroxy isoflavone (6-Methyl genistein) ..	276–78°

In all these cases the 6-methyl compounds melt much higher than their 8-methyl isomers and therefore, the product obtained by nuclear methylation of genistein should be the 6-methyl derivative (XIV *b*).

Experimental

p-*Methoxy phenyl acetonitrile*

2-Phenyl-4-anisal oxazolone[20] was obtained by heating together anisaldehyde (25 c.c.), hippuric acid (44 g.), fused sodium acetate (14 g.) and acetic anhydride (80 c.c.). Yield 45 g. The oxazolone (45 g.) was heated with aqueous sodium hydroxide (23 g. dissolved in 135 c.c. of water) for one hour. The solution was cooled, diluted with water (120 c.c.) and saturated with sulphur dioxide. The precipitated benzoic acid was filtered after 15 hours and the filtrate heated with concentrated hydrochloric acid (135 c.c.) for one hour on a water-bath. The precipitated *p*-methoxy phenyl pyruvic acid amounted to 15 g. The separation of benzoic acid from the pyruvic acid was originally effected by Cain *et al.*,[21] by fractionation of their ethyl esters. The above method is more convenient.

The oxime of the acid was prepared by heating the acid (15 g.) with aqueous sodium hydroxide (150 c.c. of 8%) and hydroxylamine hydrochloride (12 g.) for 15 minutes at 50° and acidifying the alkaline solution after 15 hours. Yield 15 g. It crystallised from dilute methanol as colourless prisms melting at 149–51° (decomp.) (Found: C, 57·1; H, 5·2; $C_{10}H_{11}O_4N$ requires C, 57·4; H, 5·3%). Baker and Eastwood[8] also prepared this compound but did not isolate and characterise it.

The dry oxime (15 g.) was heated carefully with acetic anhydride (10 c.c.) for 15 minutes at 100° and the excess of acetic anhydride decomposed with water. The acetic acid was nearly neutralised with aqueous sodium hydroxide and the nitrile extracted with ether. The ether solution was successively washed with aqueous sodium bicarbonate and water, dried over sodium sulphate and distilled. The residual oily *p*-methoxy phenyl acetonitrile (10 g.) was dried in a vacuum desiccator and used for Hoesch condensations.

Nuclear methylation of (*IX a*)

A solution of 2:4:6-trihydroxy-4′-methoxy phenyl benzyl ketone[6] (3 g.) in acetone (150 c.c.) was treated with methyl iodide (6·5 c.c.) and ignited potassium carbonate (15 g.) and the mixture refluxed in a water-bath for 3 hours. The solution was filtered off and the potassium salts were washed with hot acetone repeatedly. Acetone was distilled off from the combined filtrate. The residue was treated with water (50 c.c.) when potassium iodide dissolved. The insoluble methylated product was filtered,

washed with water and crystallised from methanol twice. 2-Hydroxy-3-methyl-4 : 6 : 4′-trimethoxy phenyl benzyl ketone (X) separated as colourless rectangular rods melting at 114–15°. Yield 0·45 g. Its alcoholic solution gave a pinkish brown colour with ferric chloride. It did not give any blue or green colour with concentrated nitric acid. It was sparingly soluble in methanol, ethyl alcohol and benzene and easily in ethyl acetate and acetone (Found: C, 68·8; H, 6·5; $C_{18}H_{20}O_5$ requires C, 68·4; H, 6·3%).

The alcoholic mother liquors on concentration and dilution with a small amount of water gave a crystalline solid. It was recrystallised twice from methanol when it was obtained as thin colourless rectangular prisms melting at 88–89° and giving a blue colour with conc. nitric acid. Yield 1·4 g. A mixed melting point with a sample of 2-hydroxy-4 : 6 : 4′-trimethoxy phenyl benzyl ketone (IX *b*)[11] was not depressed.

2 : 4 : 6-*Trihydroxy-3-methyl-4′-methoxy phenyl benzyl ketone* (*XV*)

To a solution of C-methyl phloroglucinol (V *a*)[2] (9 g.) and *p*-methoxy phenyl acetonitrile (10 g.) in dry ether (200 c.c.) was added fused zinc chloride (2 g.) and a stream of dry hydrogen chloride was passed for 5 hours through the ether solution cooled in an ice-bath. On leaving overnight, the ketimine hydrochloride separated as a heavy dark red oil. The ether layer was decanted off and the ketimine hydrochloride washed with dry ether twice and heated with water (150 c.c.) for 2 hours in a boiling water-bath. On cooling to 0°, a yellow solid separated. It was filtered and washed with water. When crystallised from dilute alcohol twice, 2 : 4 : 6-trihydroxy-3-methyl-4′-methoxy phenyl benzyl ketone crystallised as short pale yellow needles melting at 220–21°. Yield 10 g. (Found: C, 66·4; H, 5·5; $C_{16}H_{16}O_5$ requires C, 66·7; H, 5·6%). It was easily soluble in alcohol, acetone and ethyl acetate and insoluble in benzene and petroleum ether. With ferric chloride in alcoholic solution it gave a deep pink colour.

Methylation

The above ketone (1 g.) in dry acetone (100 c.c.) was heated under reflux with dimethyl sulphate (0·7 c.c.) and potassium carbonate (3 g.) for 4 hours. The potassium salts were filtered off and washed with acetone. The residue left after distilling off acetone, crystallised from methanol as colourless rectangular rods melting at 114–15° alone or when mixed with a sample of 2-hydroxy-3-methyl-4 : 6 : 4′-trimethoxy phenyl benzyl ketone (X) described earlier. Yield 0·8 g. The same product was obtained by carrying out the methylation using excess of methyl iodide in place of dimethyl sulphate.

8-*Methyl*-5 : 7 : 4′-*trimethoxy isoflavone* (*I c*)

To pulverised sodium (1 g.) cooled to 0° was added with vigorous stirring, a suspension of 2-hydroxy-3-methyl-4 : 6 : 4′-trimethoxy phenyl benzyl ketone (1 g.) in freshly distilled ethyl formate (20 c.c.) in the course of 30 minutes. The ketone was completely transferred to the reaction flask by washing with some more ethyl formate. The stirring was continued for an hour and the flask was tightly corked and left in the refrigerator. The red viscous liquid slowly set into a colourless solid mass. The cork was removed from time to time to release the pressure developed in the reaction flask. After keeping for 48 hours at 0°, pieces of ice (60 g.) were added and unreacted ethyl formate was distilled off under reduced pressure. The brown solid was filtered after cooling the mixture to 0° and washed with water. It was crystallised from methanol twice when it separated in the form of colourless thick prisms melting at 181–83°. Yield 0·6 g. It did not give any colour with alcoholic ferric chloride. It was sparingly soluble in methanol, ethyl alcohol and benzene and easily in ethyl acetate and acetone (Found: C, 70·0; H, 5·3; $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·5%).

8-*Methyl*-5 : 7 : 4′-*trihydroxy isoflavone* (8-*Methyl genistein*) (*I a*)

(i) The above trimethyl ether (I *c*) (0·85 g.) was powdered well and suspended in dry benzene (200 c.c.). Well ground anhydrous aluminium chloride (2·5 g.) was added with stirring and the mixture refluxed in a water-bath for 2 hours. The aluminium chloride complex separated as a liquid. Benzene was then distilled off completely. The residual dark viscous complex was cooled and treated with crushed ice (80 g.) and concentrated hydrochloric acid (10 c.c.) and stirred vigorously. The colourless precipitate thus obtained was filtered and washed with water. It was treated with dilute sodium carbonate solution and the undissolved oily matter was separated by filtration. The filtrate was poured into excess of hydrochloric acid. The colourless precipitate was collected and crystallised from dilute alcohol when it separated as pale yellow prisms melting at 231–32°. Yield 0·5 g. The melting point did not rise on further crystallisation. It gave a deep green colour with ferric chloride in alcoholic solution. A solution of the substance in concentrated sulphuric acid became red on the addition of a drop of concentrated nitric acid (Found: C, 65·1; H, 4·7; loss on drying *in vacuo* at 120° for 8 hours, 3·5; $C_{16}H_{12}O_5$, $\frac{1}{2}$ H_2O requires C, 65·5; H, 4·4; H_2O loss, 3·1%); Found in dried sample: C, 67·8; H, 4·6; $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2%).

(ii) 8-Methyl-5 : 7 : 4′-trimethoxy isoflavone (0·8 g.) was heated with hydriodic acid (20 c.c., *d.*, 1·7) in an oil-bath at 150° for 4 hours. To the

cooled solution was added a saturated aqueous solution of sodium bisulphite (80 c.c.). On leaving overnight, a pale yellow solid separated. It was filtered and washed with water. It was macerated with aqueous sodium carbonate (10%). Almost the whole of it dissolved. A small amount of undissolved matter was filtered and discarded. The filtrate was acidified with hydrochloric acid and the nearly colourless precipitate filtered and washed with water. 8-Methyl-5:7:4′-trihydroxy isoflavone crystallised from dilute alcohol in the form of very pale yellow irregular prisms melting at 231–32°. Yield 0·4 g. A mixed melting point with the sample obtained in (i) above was not depressed.

Remethylation

The trihydroxy compound (0·3 g.) obtained by hydriodic acid demethylation of 8-methyl-5:7:4′-trimethoxy isoflavone was dissolved in dry acetone (80 c.c.) and heated under reflux with excess of dimethyl sulphate (0·6 c.c.) and potassium carbonate (3 g.) for 30 hours. The solution was separated by filtration from the potassium salts, which were then washed with acetone. The solvent was distilled off from the combined filtrate and the residue treated with water (100 c.c.). After 48 hours, the precipitate was filtered and crystallised from alcohol. It came out as colourless prisms melting at 181–83°. It did not give any colour with alcoholic ferric chloride and a mixture of this substance with a sample of 8-methyl-5:7:4′-trimethoxy isoflavone (I *c*) also melted at 181–83°.

8-*Methyl*-5:7:4′-*triacetoxy isoflavone*

8-Methyl-5:7:4′-trihydroxy isoflavone (0·2 g.) was acetylated with acetic anhydride (5 c.c.) and few drops of dry pyridine at 140°. The triacetate was crystallised twice from acetic acid. It was obtained in the form of colourless plates and prisms melting at 213–15°. It was easily soluble in hot acetic acid (Found: C, 64·0; H, 4·7; $C_{22}H_{18}O_8$ requires C, 64·4; H, 4·4%).

The above acetate (0·12 g.) was deacetylated with a mixture of alcohol (10 c.c.) and concentrated hydrochloric acid (10 c.c.) by heating in a water-bath for 15 minutes. The crystalline precipitate obtained by dilution of the solution with water was recrystallised from dilute alcohol, when it separated as pale yellow prisms melting at 231–32° alone or when mixed with a sample of 8-methyl-5:7:4′-trihydroxy isoflavone (8-methyl genistein).

8-*Methyl*-5:4′-*dihydroxy*-7-*methoxy isoflavone* (8-*Methyl prunetin*) (*VIII b*)

8-Methyl-5:7:4′-trimethoxy isoflavone (I *c*) (1·2 g.) was dissolved in acetic anhydride (8 c.c.) and to the cooled solution was added with stirring

hydriodic acid (15 c.c., d., 1·7). The mixture was heated in an oil-bath at 110–15° for 30 minutes. It was then cooled and treated with a saturated aqueous solution of sodium bisulphite (80 c.c.). A dark sticky solid was precipitated and it became greenish yellow solid on keeping overnight. It was filtered, washed with water and thoroughly macerated with aqueous sodium carbonate (10%). Only a very small amount dissolved. The insoluble portion was filtered, washed with water and crystallised from alcohol twice. 8-Methyl prunetin separated as thick yellow rectangular prisms melting at 207–09°. Yield 0·7 g. It gave a brilliant green colour with alcoholic ferric chloride and was soluble in dilute sodium hydroxide (Found: C, 68·9; H, 5·0; $C_{17}H_{14}O_5$ requires C, 68·5; H, 4·7%).

The diacetate prepared by acetylation with acetic anhydride and pyridine, crystallised from alcohol as colourless rods and rectangular prisms melting at 161–62°.

8-Methyl-5-hydroxy-7: 4′-dimethoxy isoflavone (I b)

8-Methyl prunetin (VIII *b*) (0·3 g.) in dry acetone (100 c.c.) was treated with dimethyl sulphate (0·11 c.c., 1 mole) and ignited potassium carbonate (1·5 g.) and the mixture refluxed for 4 hours. The acetone solution was then filtered off and the solvent distilled off from the filtrate. The residue was treated with water and the precipitate filtered after 24 hours. When crystallised from alcohol twice, 8-methyl-5-hydroxy-7: 4′-dimethoxy isoflavone was obtained as clusters of colourless needles melting at 164–66°. It gave a deep green colour with alcoholic ferric chloride (Found: C, 68·8; H, 5·1; $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1%).

Summary

Okano and Beppu isolated a new isoflavone from soya bean and from its degradation reactions, they assigned to it the constitution of 8-methyl genistein. A synthesis of this compound starting from C-methyl phloroglucinol α-monomethyl ether was also reported by Shriner and Hull.

An easier method of synthesis of a compound of this structure has now been described, in which the main stage is the nuclear methylation of 2: 4: 6-trihydroxy-4′-methoxy phenyl benzyl ketone. The constitution of the product of this reaction is established by an independent synthesis from C-methyl phloroglucinol. Though this synthesis of 8-methyl genistein involves demethylation of its trimethyl ether with hydriodic acid, the absence of any rearrangement during this step has been established particularly by remethylation. The products of the present synthesis are found to be very different from the natural compound and its derivatives described by Okano

and Beppu and therefore it is considered that the natural compound cannot have the constitution assigned to it.

Partial demethylation of 8-methyl genistein trimethyl ether with hydriodic acid gives rise to 8-methyl prunetin which on partial methylation yields 8-methyl-5-hydroxy-7 : 4′-dimethoxy isoflavone. This is different from the C-monomethyl-O-dimethyl genistein obtained by Perkin and Horsfall by nuclear methylation of genistein. Therefore the product of Perkin and Horsfall may have the methyl group in the 6-position as suggested by earlier workers.

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EQUIDISTANCE AND PARALLELISM OF THE CONGRUENCES OF CURVES THROUGH POINTS OF A SUBSPACE

By R. S. Mishra

[*Department of Mathematics, Lucknow University, Lucknow (India)*]

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1. Introduction

In this paper I have considered a set of $(m-n)$ congruences of curves which are such that one curve of each congruence passes through each point of a subspace V_n of n dimensions immersed in a Riemannian manifold of m dimensions. Expressions for the angular and distantial spread vectors of one curve of a congruence with respect to the other have been found out and some theorems relating to these have been developed. Conditions necessary and sufficient that these congruences be normal have been established.

2. Congruences of Curves

Consider a V_n of co-ordinates x^i $(i = 1, \ldots, n)$ and metric $g_{ij}\,dx^i\,dx^j$ imbedded in a Riemannian V_m of co-ordinates y^α $(\alpha = 1, \ldots, m)$ and metric $a_{\alpha\beta}\,dy^\alpha\,dy\beta$, where $m > n$. In the following the letters $\alpha, \beta, \gamma, \delta, \phi, \psi$ of Greek alphabet take the values 1 to m and the letters $\mu, \nu, \sigma, \rho, \tau$ the values $n+1$ to m; while the Latin indices range from 1 to n. Assuming the metrices to be positive, we have the relations

$$g_{ij} = a_{\alpha\beta}\, y^\alpha{}_{;i}\, y^\beta{}_{;j}, \tag{2.1}$$

semi-colon (;) followed by indices denoting tensor derivatives with regard to y's or x's according as the following indices are Greek or Latin (McConnel, 1931).

If $N_{\nu|}{}^\alpha$ are the contravariant components in the y's of a system of unit vectors normal to V_n (Weatherburn, 1950, pp. 162–3),

$$a_{\alpha\beta}\, N_{\nu|}{}^\alpha\, N_{\mu|}{}^\beta = \delta_\nu{}^\mu, \tag{2.2}$$

and

$$a_{\alpha\beta}\, y^\alpha{}_{;i}\, N_{\mu|}{}^\beta = 0. \tag{2.3}$$

Also

$$\Omega_{\nu|ij} = a_{\alpha\beta}\, y^\alpha{}_{;ij}\, N_{\nu|}{}^\beta, \tag{2.4}$$

and

$$y^\alpha{}_{;ij} = \sum_\nu \Omega_{\nu|ij}\, N_{\nu|}{}^\alpha, \tag{2.5}$$

where $\Omega_{\nu|ij}$ are the components of a symmetric covariant tensor of the second order in x's.

Let us consider a set of $(m-n)$ congruences of curves which are such that a curve of each congruence passes through each point of the subspace. Suppose $\lambda_{\tau|}{}^{\alpha}$ are the contravariant components in the y's of a unit vector in the direction of a curve of a congruence, then (Mishra, 1951)

$$\lambda_{\tau|}{}^{\alpha} = t_{\tau|}{}^{l}\, y^{\alpha}{}_{;l} + \sum_{\nu} c_{\nu\tau|}\, \mathrm{N}_{\nu|}{}^{\alpha}, \tag{2.6}$$

where $t_{\tau|}{}^{l}$ are the contravariant components of a vector in the subspace and $c_{\nu\tau|}$ is a scalar, such that if $\theta_{\nu\tau|}$ is the angle between the vectors $\lambda_{\tau|}{}^{\alpha}$ and $\mathrm{N}_{\nu|}{}^{\alpha}$, then

$$\cos\theta_{\nu\tau|} = c_{\nu\tau|}, \tag{2.7}$$

and

$$1 - \sum_{\nu} \cos^2\theta_{\nu\tau|} = t_{\tau|}{}^{l}\, t_{\tau|l}. \tag{2.8}$$

Tensor derivative of (2.6) yields,

$$\lambda^{\alpha}{}_{\tau|;i} = (t_{\tau|}{}^{l}{}_{;i} - \sum_{\nu} c_{\nu\tau|}\, \Omega_{\nu|ik}\, g^{kl})\, y^{\alpha}{}_{;l} +$$

$$\sum_{\nu} (t_{\tau|}{}^{l}\, \Omega_{\nu|li} + c_{\nu\tau|;i} + \Sigma_{\mu}\, c_{\mu\tau|}\, \theta_{\nu\mu|i})\, \mathrm{N}_{\nu|}{}^{\alpha}, \tag{2.9}$$

where

$$\theta_{\mu\nu|i} = a_{\alpha\beta}\, \mathrm{N}^{\alpha}{}_{\nu|;i}\, \mathrm{N}_{\mu|}{}^{\beta}. \tag{2.10}$$

If

$$\lambda_{\tau|;i}{}^{\alpha} = q_{\tau|i}{}^{l}\, y^{\alpha}{}_{;l} + \sum_{\nu} r_{\nu\tau|i}\, \mathrm{N}_{\nu|}{}^{\alpha}, \tag{2.11}$$

then

$$q_{\tau|i}{}^{l} \equiv g^{lj} a_{\alpha\beta}\, \lambda_{\tau|;i}{}^{\alpha}\, y_{;j}{}^{\beta} = t_{\tau|}{}^{l}{}_{;i} - \Sigma_{\nu}\, c_{\nu\tau|}\, \Omega_{\nu|ik}\, g^{kl}, \tag{2.12}$$

and

$$r_{\nu\tau|i} \equiv a_{\alpha\beta}\, \lambda_{\tau|}{}^{\alpha}{}_{;i}\, \mathrm{N}_{\nu|}{}^{\beta} = t_{\tau|}{}^{l}\, \Omega_{\nu|li} + c_{\nu\tau|;i} + \Sigma_{\mu}\, c_{\mu\tau|}\, \theta_{\nu\mu|i}. \tag{2.13}$$

3. Angular Spreads

We shall now consider the angular spreads (or associate curvatures, in Bianchi's terminology) of the curves $\lambda_{\tau|}{}^{\alpha}$ with respect to the curves $\lambda_{\nu|}{}^{\alpha}$, it being supposed that $\lambda_{\tau|}{}^{\alpha}$ is parallel along $\mathrm{N}_{\nu|}{}^{\alpha}$ with respect to V_m. If their contravariant components be denoted by $\mathrm{S}^{\lambda\lambda}_{\tau\nu}{}_{|}{}^{\alpha}$, then (Graustein, 1934, p. 555).

$$\mathrm{S}^{\lambda\lambda}_{\tau\nu}{}_{|}{}^{\alpha} = \lambda_{\tau|}{}^{\alpha}{}_{;\beta}\, \lambda_{\nu|}{}^{\beta}. \tag{3.1}$$

Now,

$$\lambda_{\tau|}{}^{\alpha}{}_{;\beta}\, y^{\beta}{}_{;i} = \lambda_{\tau|}{}^{\alpha}{}_{;i}, \tag{3.2}$$

whence

$$\lambda_{\tau|}{}^{\alpha}{}_{;\beta} = \lambda_{\tau|}{}^{\alpha}{}_{;i}\, y_{;j}{}^{\gamma}\, a_{\beta\gamma}\, g^{ij}. \tag{3.3}$$

Use of (3.3) in (3.1) yields,

$$S^{\lambda\lambda}_{\tau\nu}|^{\alpha} = a_{\beta\gamma}\,\lambda\beta_{\nu|}\,y^{\gamma}_{;i}\,\lambda_{\tau|}{}^{\alpha}{}_{;i}\,g^{ij},$$

$$= t_{\nu|}{}^{i}\,\lambda_{\tau|}{}^{\alpha}{}_{;i}, \tag{3.4}$$

by virtue of (2.6).

Thus the angular spread vector of the curve $\lambda_{\tau|}$ with respect to $\lambda_{\nu|}$ is $(1-\Sigma_{\nu}\cos^2\theta_{\nu\tau|})^{\frac{1}{2}}$ times the derived vector of $\lambda_{\tau|}$ in the direction of the vector $\mathbf{t}_{\nu|}$ of the subspace.

If $\lambda_{\nu|}\beta$ are the contravariant components of a normal to the subspace, $t_{\nu|}{}^{i} = 0$, and (3.4) assumes the form

$$S^{\lambda\mathbf{N}}_{\tau\nu}|^{\alpha} = 0.$$

Hence as supposed the curves of the set of (m–n) congruences of curves such that one curve of each congruence passes through each point of the subspace V_n, are parallel with respect to the normals to the subspace.

Also since

$$S^{\mathbf{NN}}_{\tau\nu}|^{\alpha} = 0,$$

and

$$S^{\mathbf{NN}}_{\tau\tau}|^{\alpha} = 0,$$

the normals to a subspace of a Riemannian manifold are geodesics and are parallel with respect to each other.

Use of (2.11) in (3.4) yields,

$$S^{\lambda\lambda}_{\tau\nu}|^{\alpha} = t_{\nu|}{}^{i}\,(q_{\tau|i}{}^{l}\,y^{\alpha}_{;l} + \sum_{\rho} r_{\rho\tau|i}\,\mathbf{N}_{\rho|}{}^{\alpha}), \tag{3.5}$$

or with the help of (2.12),

$$S^{\lambda\lambda}_{\tau\nu}|^{\alpha} = t_{\nu|}{}^{i}\,[y^{\alpha}_{;l}\,(t_{\tau|}{}^{l}{}_{;i} - \sum_{\mu} c_{\mu\tau|}\,\Omega_{\mu|ik}\,g^{kl}) +$$

$$\sum_{\rho} \mathbf{N}_{\rho|}{}^{\alpha}\,(t_{\tau|}{}^{l}\,\Omega_{\rho|li} + c_{\rho\tau|;i} + \sum_{\mu} c_{\mu\tau|}\,\theta_{\rho\mu|i})]. \tag{3.6}$$

Thus (3·5) and (3·6) are other expressions for the angular spread vector of the curve $\lambda_{\tau|}$ with respect to $\lambda_{\nu|}$.

The resolved part of the angular spread vector of the curve $\lambda_{\tau|}$ with respect to $\lambda_{\nu|}$ along a normal $\mathbf{N}_{\sigma|}$ to the subspace is given by

$$a_{\alpha\beta}\,S^{\lambda\lambda}_{\tau\nu}|^{\alpha}\,\mathbf{N}_{\sigma|}\beta = t_{\nu|}{}^{i}\,r_{\sigma\tau|i}. \tag{3.7}$$

The equation (3.7) gives another interpretation for $r_{\sigma\tau|i}$.

Similarly $$a_{\alpha\beta}\,S^{\lambda\lambda}_{\tau\nu}|^{\alpha}\,y^{\beta}_{;l} = t_{\nu|}{}^{i}\,q_{\tau|il}, \tag{3.8}$$

and (3·8) gives another meaning for $q_{\tau|il}$.

Putting $\nu = \tau$ in (3.4), (3.5) and (3.6) we get the contravariant components of the first curvature vector of the curve $\lambda_{\tau|}$. The square of the first curvature vector of the curve $\lambda_{\tau|}$ is given by

$$a_{\alpha\beta}\, S^{\lambda\lambda}_{\tau\tau}|^{\alpha}\, S^{\lambda\lambda}_{\tau\tau}|^{\beta} = a_{\alpha\beta}\,(q^{j}_{\tau|i}\, y^{\alpha}_{;j} + \sum_{\rho} r_{\rho\tau|i}\, N_{\rho|}{}^{\alpha})\,(q_{\tau|j}{}^{m}\, y^{\beta}_{;m} + \sum_{\sigma} r_{\sigma\tau|j}\, N_{\sigma|}{}^{\beta})\, t_{\tau|}{}^{i}\, t_{\tau|}{}^{j}$$

$$= (q^{j}_{\tau|i}\, q_{\tau|j}{}^{m}\, g_{lm} + \sum_{\rho} r_{\rho\tau|i}\, r_{\rho\tau|j})\, t_{\tau|}{}^{i}\, t_{\tau|}{}^{j}. \tag{3.9}$$

Substitutions from (2.12) and (2.13) give other expressions for the first curvature vector of the curve $\lambda_{\tau|}$.

The necessary and sufficient condition that the curve $\lambda_{\tau|}$ is a geodesic is obtained by equating the right-hand member of (3.9) *to zero.*

The contravariant components of angular spread vector of the normal $N_{\tau|}$ to the subspace with respect to $\lambda_{\nu|}$ is given by

$$S^{N\lambda}_{\tau\nu}|^{\alpha} = N_{\tau|}{}^{\alpha}{}_{;i}\, t_{\nu|}{}^{i}, \tag{3.10}$$

which cannot vanish unless the vector $\lambda_{\nu|}$ is normal to the subspace. Thus we see that *though the vector $\lambda_{\nu|}$ is parallel with respect to the normal $N_{\tau|}$, the converse is not true, in general.*

Since (Weatherburn, 1950, p. 170),

$$N_{\tau|}{}^{\alpha}{}_{;i} = -\,\Omega_{\tau|ik}\, g^{kj}\, y^{\alpha}{}_{;j} + \sum_{\mu} \theta_{\mu\tau|i}\, N_{\mu|}{}^{\alpha}, \tag{3.11}$$

the equation (3.10) assumes the form

$$S^{N\lambda}_{\tau\nu}|^{\alpha} = -\,\Omega_{\tau|ik}\, g^{kj}\, t_{\nu|}{}^{i}\, y^{\alpha}{}_{;j} + \sum_{\mu} \theta_{\mu\tau|i}\, N_{\mu|}{}^{\alpha}\, t_{\nu|}{}^{i}. \tag{3.12}$$

This is another expression for $S^{N\lambda}_{\tau\nu}|^{\alpha}$.

4. Distantial Spread Vector of $\lambda_{\tau|}$ and $\lambda_{\nu|}$

If we denote by $T^{\lambda\lambda}_{\tau\nu}|^{\alpha}$ the contravariant components of distantial spread vector (Graustein, 1934) of the curves $\lambda_{\tau|}$ and $\lambda_{\nu|}$, then

$$T^{\lambda\lambda}_{\tau\nu}|^{\alpha} = S^{\lambda\lambda}_{\tau\nu}|^{\alpha} - S^{\lambda\lambda}_{\nu\tau}|^{\alpha}, \tag{4.1}$$

$$= \lambda_{\tau}{}^{\alpha}{}_{|;\beta}\, \lambda_{\nu|}{}^{\beta} - \lambda_{\nu|}{}^{\alpha}{}_{;\beta}\, \lambda_{\tau|}{}^{\beta}. \tag{4.2}$$

Since $$S^{\lambda N}_{\nu\tau}|^{\alpha} = 0,$$

$$T^{N\lambda}_{\tau\nu}|^{\alpha} = S^{N\lambda}_{\tau\nu}|^{\alpha}, \tag{4.3}$$

and $$T^{\lambda N}_{\tau\nu}|^{\alpha} = -\,S^{N\lambda}_{\nu\tau}|^{\alpha}. \tag{4.4}$$

Hence *the distantial spread vector of a normal to the subspace V_n of a V_m, with respect to a curve $\lambda_{\nu|}$ of the congruence is the same as its angular spread vector with respect to the same curve $\lambda_{\nu|}$.*

The sum of the distantial spread vector of a curve $\lambda_{\tau|}$ of the congruence with respect to a normal $\mathbf{N}_{\nu|}$ to the subspace, and the angular spread vector of the normal $\mathbf{N}_{\nu|}$ with respect to the curve $\lambda_{\tau|}$ vanishes.

By virtue of (3.5) the equation (4.1) assumes the form

$$\mathrm{T}^{\lambda\lambda}_{\tau\nu}|^{\alpha} = y^{\alpha}{}_{;l}\,(t_{\nu|}{}^{i}\,q_{\tau|i}{}^{l} - t_{\tau|}{}^{i}\,q_{\nu|i}{}^{l}) + \sum_{\mu}(t_{\nu|}{}^{i}{}_{;j}\,r_{\mu\tau|i} - t_{\tau|}{}^{i}\,r_{\mu\nu|i})\,\mathrm{N}_{\mu|}{}^{\alpha}, \tag{4.5}$$

where $q^{l}_{\tau|i}$ and $r_{\mu\tau|i}$ are given by (2.12) and (2.13).

(4.5) *is another expression for* $T^{\lambda\lambda}_{\tau\nu}|^{\alpha}$.

From (4.5) it is obvious that

$$\mathrm{T}^{\mathrm{NN}}_{\tau\nu}|^{\alpha} = 0.$$

Hence *the distantial spread vector between any two normals of a subspace V_n immersed in V_m is a null vector.*

Also, a set of normals to a subspace V_n immersed in V_m are equidistant with regard to each other.

5. Condition For A Normal Congruence

We shall now find the condition that the congruence of curves $\lambda_{\tau|}$ be normal. We know that the necessary and sufficient condition for this is (Weatherburn, 1950, p. 103),

$$a_{\alpha\phi}\,\lambda_{\tau|}{}^{\phi}\,(a_{\beta\delta}\,\lambda_{\tau|}{}^{\delta}{}_{;\gamma} - a_{\gamma\delta}\,\lambda_{\tau|}{}^{\delta}{}_{;\beta}) + a_{\beta\phi}\,\lambda_{\tau|}{}^{\phi}\,(a_{\gamma\delta}\,\lambda_{\tau|}{}^{\delta}{}_{;\alpha} - a_{\alpha\delta}\,\lambda_{\tau|}{}^{\delta}{}_{;\gamma})$$
$$+ a_{\gamma\phi}\,\lambda_{\tau|}{}^{\phi}\,(a_{\alpha\delta}\,\lambda_{\tau|}{}^{\delta}{}_{;\beta} - a_{\beta\delta}\,\lambda_{\tau|}{}^{\delta}{}_{;\alpha}) = 0. \tag{5.1}$$

Use of (3.3) in this equation yields,

$$\lambda_{\tau|}{}^{\phi}\,\lambda_{\tau|}{}^{\delta}{}_{;i}\,y^{\psi}{}_{;j}\,g^{ij}\,[a_{\alpha\phi}\,(a_{\beta\delta}\,a_{\gamma\psi} - a_{\gamma\delta}\,a_{\beta\psi}) + \text{two other terms in which}$$
$$\alpha, \beta, \gamma \text{ take the values cyclically}] = 0. \tag{5.2}$$

By virtue of (2.6) and (2.12) the condition (5.2) can also be written as

$$(t_{\tau|}{}^{l}\,y^{\phi}{}_{;l} + \Sigma_{\nu}\,c_{\nu\tau|}\,\mathrm{N}_{\nu|}{}^{\phi})\,(q_{\tau|i}{}^{l}\,y^{\delta}{}_{;l} + \sum_{\mu} r_{\mu\tau|i}\,\mathrm{N}_{\mu|}{}^{\delta})\,y^{\psi}{}_{;j}\,g^{ij}\times$$
$$[a_{\alpha\phi}\,(a_{\beta\delta}\,a_{\gamma\psi} - a_{\gamma\delta}\,a_{\beta\psi}) + \text{two other similar terms with}$$
$$\alpha, \beta, \gamma \text{ occurring cyclically}], \tag{5.3}$$

where $q_{\tau|i}{}^{l}$ and $r_{\nu\tau|i}$ are given by (2.12) and (2.13) respectively.

6. MUTUALLY ORTHOGONAL CURVES

Let $(m-n)$ curves of a congruence $\lambda_{\tau|}$ be mutually at right angles. Then the values of Ricci's coefficients of rotation $\gamma_{\rho\mu\nu|}$ are given by (Weatherburn, 1950, p. 99).

$$\gamma_{\rho\mu\nu|} = a_{\alpha\gamma}\,\lambda_{\rho|;\beta}{}^{\gamma}\,\lambda_{\mu|}{}^{\alpha}\,\lambda_{\nu|}{}^{\beta}. \tag{6.1}$$

Use of (3.3) in this equation yields,

$$\begin{aligned}\gamma_{\rho\mu\nu|} &= a_{\alpha\gamma}\,\lambda_{\mu|}{}^{\alpha}\,\lambda_{\nu|}{}^{\beta}\,\lambda_{\rho|}{}^{\gamma}{}_{;i}\,y^{\delta}{}_{;j}\,a_{\beta\delta}\,g^{ij},\\ &= a_{\alpha\gamma}\,\lambda_{\rho|}{}^{\gamma}{}_{;i}\,\lambda_{\mu|}{}^{\alpha}\,t_{\nu|j}\,g^{ij},\end{aligned} \tag{6.2}$$

by virtue of (2.6).

The equation (6.2) shows that if $\lambda_{\nu|}$ is a normal to the subspace

$$\gamma_{\rho\mu\nu} = 0.$$

It is to be noted that even if one of the curves $\lambda_{\nu|}$ is normal to the subspace and all other curves are mutually at right angles, the other curves may not be normal to the subspace.

The necessary condition that the curves of the congruence $\lambda_{\tau|}$ be geodesics is given by

$$\gamma_{\rho\tau\tau|} = 0\,. \quad (\rho = n+1, \ldots . m). \tag{6.3}$$

By virtue of (6·1) and (6·2) this condition reduces to

$$a_{\alpha\gamma}\,\lambda_{\tau|}{}^{\alpha}\,\lambda_{\rho|}{}^{\gamma}{}_{;\beta}\,\lambda_{\tau|}{}^{\beta} = 0, \tag{6.4}$$

or
$$a_{\alpha\gamma}\,\lambda_{\tau|}{}^{\alpha}\,\lambda_{\rho|}{}^{\gamma}{}_{;i}\,t_{\tau|j}\,g^{ij} = 0, \tag{6.5}$$

or by virtue of (2.11),

$$a_{\alpha\gamma}\,(q_{\rho|i}{}^{l}\,y^{\gamma}{}_{;l} + \sum_{\nu} r_{\nu\rho|i}\,\mathrm{N}_{\nu|}{}^{\gamma})\,\lambda_{\tau|}{}^{\alpha}\,t_{\tau|j}\,g^{ij} = 0, \tag{6.6}$$

or
$$(q_{\rho|i}{}^{l}\,t_{\tau|l} + \sum_{\nu} r_{\nu\rho|i}\,c_{\nu\tau|})\,t_{\tau|}{}^{i} = 0, \tag{6.7}$$

by virtue of (2.6).

(6.3) is clearly satisfied by the normals $\mathrm{N}_{\tau|}$.

The condition (6.7) can further be written in the form

$$\begin{aligned}t_{\tau|}{}^{i}\,[t_{\tau|l}\,(t_{\rho|}{}^{l}{}_{;i} - \sum_{\nu} c_{\nu\rho|}\,\Omega_{\nu|ik}\,g^{kl}) + \sum_{\nu}(t_{\rho|}{}^{l}\,\Omega_{\nu|li} + c_{\nu\rho|;i}\\ + \sum_{\mu} c_{\mu\rho|}\,\theta_{\nu\mu|i})\,c_{\nu\tau|}] = 0.\end{aligned} \tag{6.8}$$

It may be noted in this connection that the conditions (6.3) to (6.8) are only the necessary conditions. They are not sufficient.

The expression on the left of (6·4) is the tendency of the vector $\lambda_{\rho|}$ in the direction of the vector $\boldsymbol{\lambda}_{\tau|}$. *Hence if a curve of the congruence* $\lambda_{\tau|}$ *is geodesic the tendencies of all other mutually orthogonal curves of the congruence is zero.* This condition again is not sufficient.

If (5.1) is multiplied by $\lambda_{\mu|}{}^{\alpha}\,\lambda_{\nu|}{}^{\gamma}$ and summed for α and γ, the condition (5.1) that the congruence $\lambda_{\tau|}$ be normal, reduces to

$$\gamma_{\tau\mu\nu|} = \gamma_{\tau\nu\mu|}.$$

It may be noted here that τ, μ ν are unequal.

If all the curves of the congruence are normal, we must have

$$\gamma_{\tau\mu\nu|} = 0.$$

In that case the curves of the congruence will be a set of normals to the subspace.

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